PB-242 174

ANALYSIS OF EMISSIONS FROM OUTBOARD TWO CYCLE MARINE ENGINES

W. J. Weber, Jr., et al

Boating Industry Associations

Prepared for:

National Environmental Research Center
Michigan University

June 1975

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-670/2-75-061

2.

PB 242 174

4. TITLE AND SUBTITLE
ANALYSIS OF EMISSIONS FROM OUTBOARD TWO CYCLE MARINE ENGINES

5. REPORT DATE
June 1975 (Issuing Date)

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
W. J. Weber, Jr., D. E. Cole, and J. C. Posner

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Environmental and Water Resources Engineering
Laboratory and the Automotive Engineering Laboratory
The University of Michigan
Ann Arbor, Michigan 48104

10. PROGRAM ELEMENT NO.
1BB038

11. XXXXXXXT/GRANT NO.
R-801799

12. SPONSORING AGENCY NAME AND ADDRESS
National Environmental Research Center
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES
See also EPA-670/2-75-062, EPA-670/2-75-063, and EPA-670/2-75-064

16. ABSTRACT

The work herein reported is the University of Michigan's contribution to a larger scope study dealing with the environmental impacts of outboard engine usage on small lake systems. This part of the total project is concerned with laboratory investigations, two other groups being involved with field studies. A wide variety of two-stroke engines were run under load conditions and the emissions, both condensable and noncondensables, analyzed. The influence of maintenance on emissions was also examined and found to have little effect. Crankcase drainage constituted only a small fraction of the total hydrocarbons emitted and was enriched in oil over the fuel. Exhaust products which one could reasonably expect to be condensable in a water-column constituted less than 10% of fuel fed in all cases and usually considerably less. The major portion of the water condensable aromatics evaporated fairly rapidly from the receiving water, but a portion was non-volatile. Analytical methods for field study were developed and the toxicity of both condensed exhaust and individual compounds in gasoline to goldfish were determined. This report was submitted in fulfillment of Project Number 15020 GPG and Grant Number 801799 by the University of Michigan under the partial sponsorship of the Environmental Protection Agency. Work was completed as of August 31, 1973.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Outboard engines	Crankcase drainage	13B
Motor boats	Outboard motor emissions	
Gas analysis	Oil pollution	
Chemical tests	Physical characteristics	
Physical properties	Chemical characteristics	
Sampling		
Lakes		

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18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
266

22. PRICE
$8.50-2.25

EPA Form 2220-1 (9-73)

1 67 113

EPA-670/2-75-061
June 1975

PB242174

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Program Element No. 1BB038

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CINCINNATI, OHIO 45268

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REVIEW NOTICE

The National Environmental Research Center, Cincinnati, has reviewed this report and approved it for publication in order that the data may be made widely available and serve as a basis for future studies by others, should they be desired. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for their use.

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water and land. The National Environmental Research Centers provide the multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

The northern lakes, southern lakes and laboratory studies were conducted by independent consultants who were subcontractors to the Boating Industry Associations. The project design was approved by the U. S. Environmental Protection Agency and monitored during the course of the study by EPA personnel. As a result of the studies and the contractors' analysis of the data, no significant environmental impacts from outboard motor boating activity were found under the study conditions. However, since it was impossible in this study to cover fully all the diverse factors which may be impacted by emissions from outboard motors, care should be taken in extrapolating the results to situations other than those covered by this specific study. These data are being presented in order that they may be widely available and serve as a basis for possible future studies by others should they be required in considering the implementation of regulations relating to the recreational utilization of the Nation's waters.

A. W. Breidenbach, Ph.D.
Director
National Environmental Research
Center, Cincinnati

ABSTRACT

The work herein reported is the University of Michigan's contribution to a larger scope study dealing with the environmental impacts of outboard engine usage on small lake systems. This part of the total project is concerned with laboratory investigations, two other groups being involved with field studies.

A wide variety of two-stroke engines were run under load conditions and the emissions, both condensable and non-condensables, analyzed. The influence of maintenance on emissions was also examined and found to have little effect. Crankcase drainage constituted only a small fraction of the total hydrocarbons emitted and was enriched in oil over the fuel. Exhaust products which one could reasonably expect to be condensable in a water-column constituted less than 10% of fuel fed in all cases and usually considerably less. The major portion of the water condensable aromatics evaporated fairly rapidly from the receiving water, but a portion was non-volatile. Analytical methods for field study were developed and the toxicity of both condensed exhaust and individual compounds in gasoline to goldfish were determined.

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ACKNOWLEDGEMENT

The principal investigators acknowledge the project research assistants, Dr. Gary Brenniman, Mr. Charles Delos, Dr. Hans Posselt, Mr. Marion Vande Steeg, and Ms. Lucianna Yu, for their contributions in performing the work described herein. We also thank the manufacturers of the outboard engines tested in this research for their cooperation in supplying the engines and pertinent technical data.

SECTION I

CONCLUSIONS

1. Gas-phase carbon monoxide concentrations were closely related to the fuel/air ratio supplied by the carburetor, and ranged from less than 2% at 1,000 rpm for a 6 hp Evinrude engine to greater than 9.5% at 3,000 rpm for a 35 hp Chrysler engine.

2. Gas-phase carbon dioxide concentrations ranged from a low of approximately 3.5% to more than 9.5%, and were also principally a function of the fuel/air ratio.

3. No trend with speed and load was observed for either carbon monoxide or carbon dioxide emissions.

4. Total (FID) gas-phase hydrocarbon emission concentrations ranged from a low of 4500 ppm measured as C_6H_{14} to a high of 10,000 ppm as C_6H_{14}. These concentrations, attributable to over-scavenging, which in turn is related to engine trapping efficiency, generally decreased with increasing speed and load.

5. NDIR gas-phase hydrocarbon concentrations were substantially lower than FID hydrocarbon concentrations because of the relatively inferior response of NDIR analyzers.

6. Engine trapping efficiency ranged from approximately 50% to greater than 80%, and in general was observed to increase with engine speed and load.

7. Mass emission rates of both carbon monoxide and unburned hydrocarbons increased with increasing speed and load in the test engines. For example, the total hydrocarbon emissions ranged from less than 0.02 kg/hour for an Evinrude 6 hp engine at 1,000 rpm (0.2 bhp) to approximately 3 kg/hour for a 105 hp Chrysler engine at 4,000 rpm (50 bhp).

8. The composition of the gas-phase exhaust hydrocarbons resembled the composition of the fuel with the principal exceptions that the olefin concentration was greater and the paraffin concentration slightly less than in the test fuel. A moderate variation in composition was evident from engine to engine.

9. The condensable material from outboard engine exhaust was found to contain paraffinic, olefinic and aromatic hydrocarbons as well as small amounts of phenols and carbonyl compounds.

10. The composition of the condensate was very similar to that of the fuel. Aromatic compounds constitute 20-25% of the total condensed hydrocarbon amount. Toluene is slightly lower on a percentage basis in the condensate than in the fuel, and binuclear aromatics are slightly higher.

11. The total amount of condensable material which can reasonably be expected to be condensed in a boating situation varied from about 1.5-7% of the fuel used.

12. Three engines were investigated for crankcase drainage; all exhibited the general trend of decreasing drainage with increasing engine speed and load.

13. At low speed and load test conditions the spread of the drainage results were relatively large. For example, at 1,500 rpm the drainage for an 18 hp Evinrude was approximately 75 grams per hour whereas drainage from a 35 hp Chrysler was in excess of 275 grams per hour. At the 1500 rpm test condition drainage, expressed as a percent of the fuel used, ranged from 3% for a 50 hp Mercury to in excess of 8% for a 35 hp Chrysler engine.

14. The oil composition of the crankcase drainage was about 20-30%. Since the ratio of oil to gasoline in the fuel was 1:50, crankcase drainage represents a 10-15 fold increase in oil content over the mixture fed to the engine.

15. Maintenance in the form of a conventional "tune up" had

little influence on either the gaseous or condensable emission characteristics of two field engines tested.

16. The aromatic constituents of the condensate have an evaporation half-life of about 11 days in a lake or other water body, assuming, conservatively, a quiescent body of water at 20 °C, the condensate being uniformly distributed initially to a depth of one meter.

17. There is a small, non-volatile hydrocarbon fraction which is not removed by evaporation from water exposed to submerged two-cycle engine exhaust emissions.

18. 96-hour LC-50 values for goldfish mortality were determined in dynamic bioassay tests as 22.8 ppm for pure toluene, 16.9 for xylene, and 9-10 ppm as toluene for outboard engine condensate.

19. The standard carbon-chloroform extract method for determination of organics in water proved unsuitable for determining the aromatic hydrocarbon content of water exposed to heavy outboard engine use in the associated field studies.

20. The use of a weakly basic macroreticular ion exchange resin was shown to be far superior for concentration of aromatic hydrocarbons from field samples.

21. An alternative method, the use of spectro-grade cyclohexane extraction for determination of aromatic hydrocarbons, gave results comparable to the resin technique.

SECTION II

RECOMMENDATIONS

It is recommended that one related area which bears on the problem of the fate of outboard exhaust components condensed in the water-column but which was outside the immediate scope of this project, be investigated. The research area proposed would relate to the role of sedimentary material in the removal of exhaust components from the aqueous phase. The impact of this mechanism would obviously depend on such factors as turbidity of the receiving water, depth and composition of the bottom, water temperature, etc., but such a study would answer the one unresolved question, namely the rate of removal and ultimate fate of the non-volatile organics contributed to the aqueous system through outboard engine usage.

SECTION III

INTRODUCTION

Environmental quality has become an issue of National concern; concern relating to the spectrum of environmental problems associated with a technologically advanced society. Significant legislation mandating improvement in environmental quality has been brought forward. Important sources of air and water pollution have been identified and brought under increased control. As the impacts of major sources of pollution have been reduced, those of lesser significance have become of greater relative import. Against this backdrop, interest has developed in careful examination of potential air and water pollution effects of two-cycle outboard marine engines. Previous studies have shown that a potential for affecting the aquatic environment adversely as a result of outboard engine usage does exist (1-7). However, data on the magnitude of the impact in a realistic usage situation are lacking.

The purpose of this study has been, therefore, assessment of the outboard engine as a source of environmental pollution, with particular emphasis on potentially adverse impacts on the aquatic eco-system.

The research covered in this report represents one part of a three part study which comprised the overall project. The other research groups involved were Environment Engineering, Inc. (E.E.I.) of Gainesville, Florida and Environmental Control Technology, Inc. (ENCOTEC) of Ann Arbor, Michigan, these subprojects being called respectively the Southern field studies project and the Northern field studies project.

The University of Michigan was primarily concerned with laboratory studies, although the development of special analytical methods, notably the determination of trace amounts of hydrocarbons in water, for use by the field studies groups was also included.

Mechanical operation and testing of all engines studied, analyses of gaseous exhaust emissions, and collections of crankcase drainage and condensable fractions, were conducted at the University's Automotive Engineering Laboratory. Analyses of fractions of exhaust emissions that might be trapped in a water body (condensables), crankcase drainage, evaporation rates, certain analyses from field studies associated with other segments of the project, and laboratory fish toxicity studies were conducted at the Environmental and Water Resources Engineering Laboratory.

SECTION IV

ENGINE TESTING AND GAS PHASE EMISSIONS

INTRODUCTION

A total of 14 engines was initially selected for emission evaluation. Included were engines covering a broad range of horsepower from the four major American manufacturers. All were of the two-stroke design. Becasue early test results showed that the emission characteristics of the various engines were similar on a concentration basis, the scope of the initial project was reduced in terms of the total number of engines tested. However, two additional assignments, crankcase drainage and maintenance studies, broadened the scope of the project.

The test facility and personnel capability was developed over a period of five years at the University of Michigan. During this period Outboard Marine Corporation sponsored research on the emission characteristics of their two-cycle engines (8-10). This experience was directly applicable to the current study, and in fact, markedly reduced the normal start-up delay of the project.

The problems encountered during collection and analysis of the exhaust gas from the two-cycle engine are much more formidable than found with the conventional four-cycle automotive engines that have been so thoroughly investigated over the past 25 years (11-14). These problems are amplified by the lack of prior published art and emphasized the value of the early University of Michigan work. Several experimental techniques were developed in the context of the project. The condensate apparatus for collections of exhaust condensables is of major significance and is discussed in an ensuing section of this report.

In general the engines performed remarkably well on the test stand. The various gaseous exhaust emissions measured included unburned hydrocarbons, carbon monoxide, carbon dioxide, and oxygen. In addition, a subtractive column technique was used to separate hydrocarbons into major family constituents.

Several major differences between the two-cycle outboard engine and the conventional four-cycle automotive engine, which is the natural basis for comparison, were noted:

1. hydrocarbon emissions are more than an order of magnitude greater;
2. the carbon monoxide emissions are substantially higher, because the air-fuel mixture ratio used is approximately three ratios greater;

3. the exhaust contains substantial oxygen; and
4. the exhaust hydrocarbons are more highly parafinic and resemble the fuel more closely.

The major source of the hydrocarbon emissions was found to be over-scavenging or short-circuiting of the fuel-air mixture during the scavenging process.

TESTING AND ANALYTICAL PROCEDURES

Test Engines and Associated Instrumentation

Initially 17 different engines were consigned to the University of Michigan by the Outboard Marine Corporation, Mercury, Chrysler and Tecumseh Products. The engines selected for testing represented samples from a variety of two-stroke engine configurations. They ranged in size from 3.6 hp to 105 hp and represented a spectrum of engines from four manufacturers. Of the initial group of engines, only 12 were actually tested because results showed that additional testing would probably be redundant, with little chance of obtaining additionally important data. Two "maintenance" engines were added, bringing the total number of engines tested to 14. The crank-case designs included closed, recirculating and drained types. The ignition systems represented both the conventional and high-voltage capacitive-discharge (CD) systems. Two of the engines tested were air-cooled, the rest were water-cooled. Carburetion varied both with manufacturer and engine size.

The engines, together with a number of pertinent specifications, are identified in Table 1. Each engine was instrumented and fitted with exhaust gas sample probes. An additional 50 hp Mercury was disassembled in order to use its "long shaft" lower unit on the 50 hp Mercury engine(s) listed in Table 1.

Testing was conducted in the University of Michigan Automotive Laboratory using both a motoring-generating dynamometer and test tank.

Large Engines - Dynamometer Installation

The larger engines (35 hp to 105 hp) were mounted on a special test stand on loan from the Outboard Marine Corporation and coupled to a 120 hp General Electric dynamometer.

The engine prop shaft was coupled to the dynamometer shaft using a specially built collar with shear pins at each end. Since two-stroke engines characteristically exhibit moderate misfire at low speeds, extended operation at low speed caused occasional failure of the pins. For this reason the minimum engine speed used for the long

TABLE 1

TEST ENGINES AND SPECIFICATIONS*

Brand Name	Rated hp	@ RPM	Model Number	Serial Number	No. of Cyl.	Dis-placement (cu.in)	Gear Ratio	Cooling System	Crankcase Drain	Fuel/ Oil Ratio
Chrysler	105	5000	1057 HC	9994	4	96.55	15/26	Water	Recycled	50/1
Mercury	50	5300	500E	3170501	4	43.8	1/2	Water	Recycled	50/1
Chrysler	35	4750	350HD	1053	2	35.9	13/22	Water	Recycled	50/1
Chrysler	12.9	5000	122HA	3725	2	13.62	14/22	Water	Recycled	50/1
Mercury	7.5	5500	75	3196951	2	10.9	1/2	Water	Recycled	50/1
Eska	7.0	5650	1747A	153145	1	7.5	14/21	Air & Water	Closed	24/1
Chrysler	3.6	4500	32HB	6346	1	5.18	14/21	Air & Water	Closed	16/1
Evinrude	6	4500	6202DJ	03899	2	884	15/26	Water	Recycled	50/1
Evinrude	18	4500	18202R	E03098	2	22.0	12/21	Water	Recycled	50/1
Chrysler	35	4750	355HC	6336	2	35.9	13/21	Water	Drained	50/1
Evinrude	18†	4500	18202R	E03098	2	220	12/21	Water	Drained	50/1
Mercury	50†	5300	500E	3170501	4	43.8	1/2	Water	Drained	50/1

† Modified to a drained engine   * Field engines tested are not included in this table

duration condensate collection runs was 1500 rpm. Safety considerations dictated a maximum engine speed of 4000 rpm for the large engines since the operators were in the test cell with the engines.

The lower unit gearcase was immersed in a circulating water bath built into the test stand. Cooling water was supplied to the engine from a constant head overflow device mounted to the bedplate next to the engine. Water was introduced through modified flushing adapters. The lower section of the stand into which the engine exhausted was completely surrounded with a sheet aluminum casing. The laboratory exhaust system was plumbed into this volume to facilitate removal of exhaust. A front view of a 35 hp Chrysler on the dynamometer test stand is shown in Figure 1. The dynamometer control panel is shown in Figure 2. Engine speed was measured with a conventional magnetic pick-up and electronic-counter arrangement that is a standard component of the dynamometer system.

Fuel was delivered to all test engines (tank and dynamometer) from the standard auxiliary fuel tanks furnished with the engines. Mass flow of the fuel was obtained by measuring the initial and after-test fuel and fuel tank weight. An Ohaus heavy-duty solution balance with an accuracy of ±0.5 gram was used for this measurement. Since

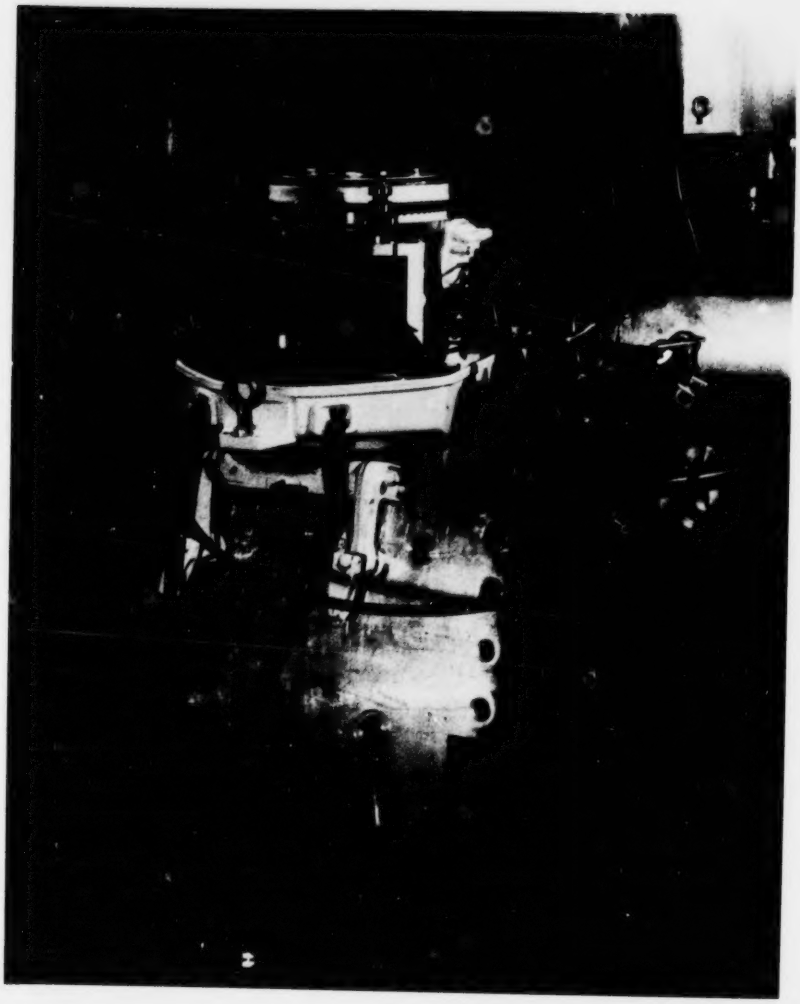

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Figure 1 Front View of the 35 HP Chrysler Engine Installed on the Test Stand

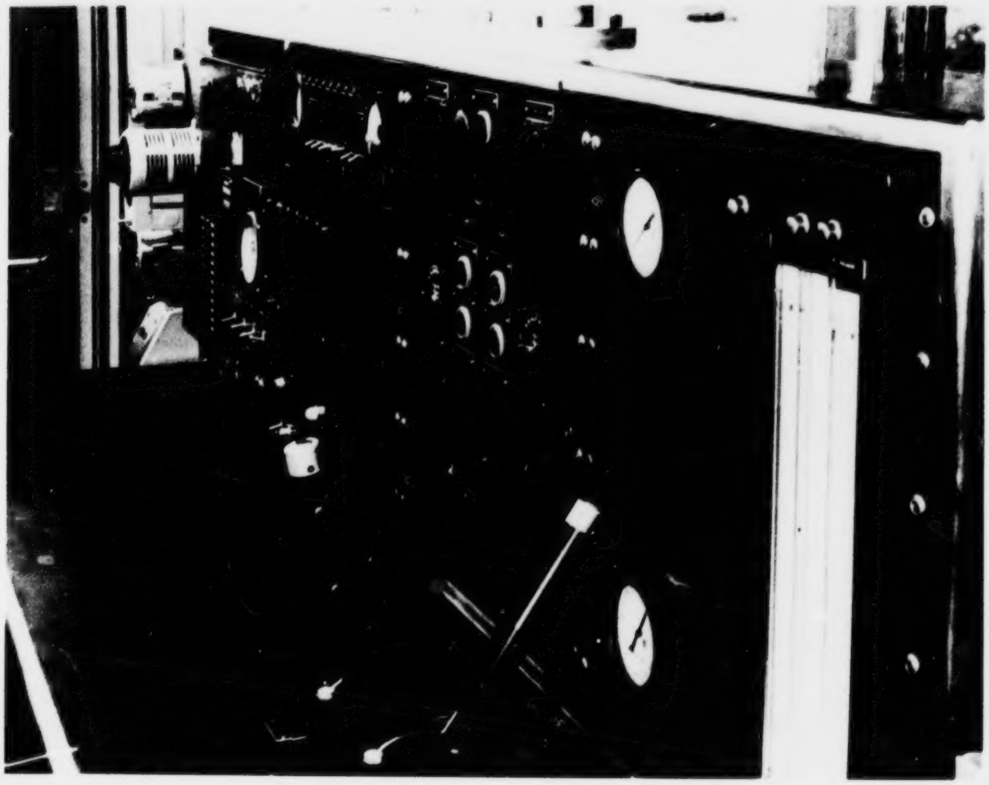

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Figure 2 Dynamometer Control Panel

each test was run at a constant speed and load, it was not necessary to continuously monitor the fuel rate. Any change in engine operation was readily detected from the continuously monitored exhaust emission data.

Small Engines - Test Tank

These engines (3.6 hp to 18 hp) were operated in a test tank (3' x 4' x 4') and were loaded using test propellors (props). These props were designed to maintain the rated rpm at wide-open throttle. The OMC and Chrysler engines were supplied with tank props which served this purpose effectively. The Eska and Sears engines were loaded by a prop that consisted of a flat aluminum disc with a number of holes drilled through it at various radii from the center. A sample of this design is shown in Figure 3 for the 4.5 and 7.0 hp Sears engines. The number and size of the holes determined the magnitude of loading. The 7.5 hp Mercury engine utilized a through-prop exhaust system. Consequently a standard three-blade prop was cut down and used as a tank prop. In addition the engine was placed near the center of the tank to eliminate the cavitation problems observed in the initial testing.

A water overflow and supply system permitted the maintenance of a constant level of fresh water in the tank.

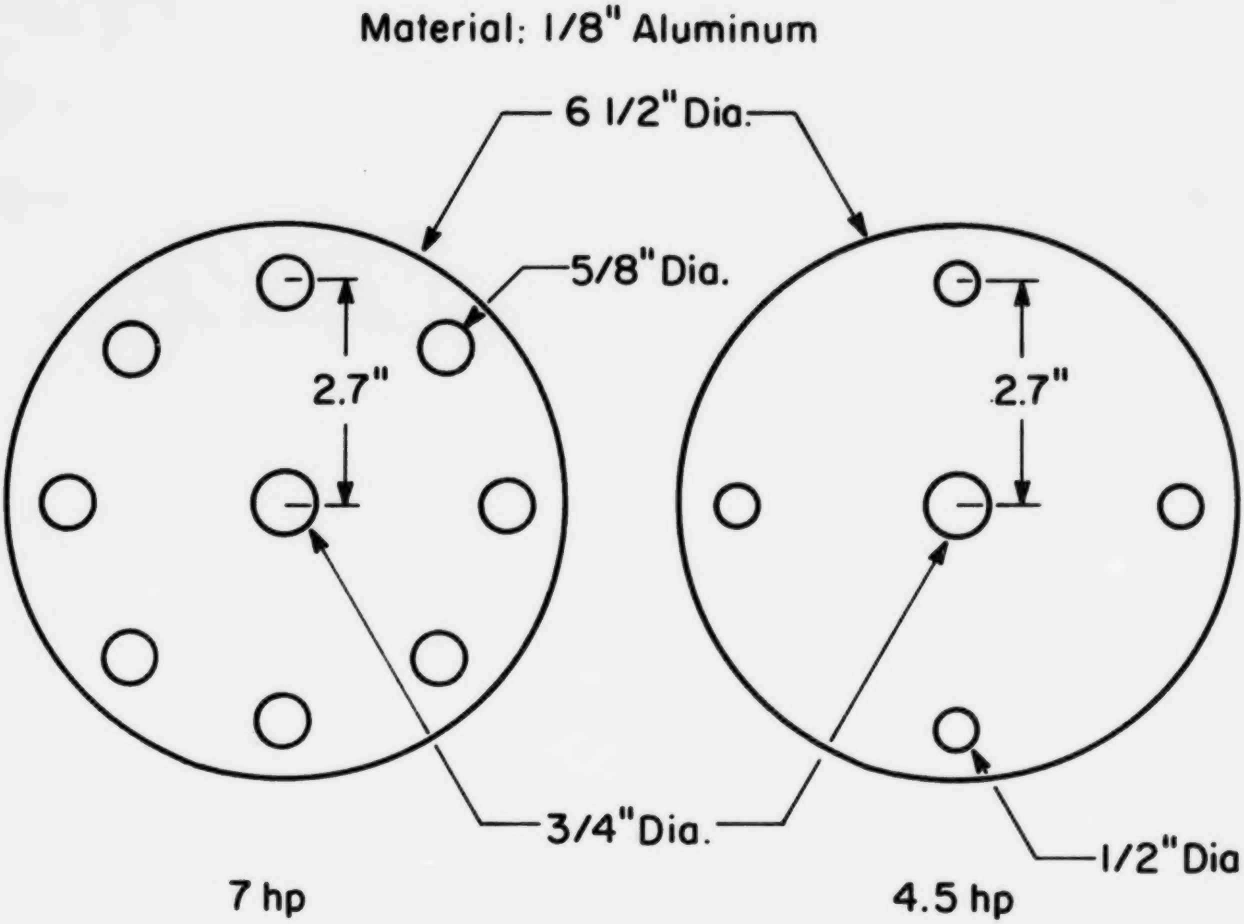
Material: 1/8" Aluminum
6 1/2" Dia.
5/8" Dia.
2.7"
2.7"
3/4" Dia.
1/2" Dia
7 hp
4.5 hp

Figure 3 Test Prop Design Used on 7 and 4.5 HP Sears Air-Cooled Engines.

Water was circulated through the engine by the engine's water pump and in the tank by the prop. A 12.9 hp Chrysler engine mounted on the tank together with associated equipment is shown in Figure 4.

Two of the engines tested were air-cooled Chrysler 3.6 hp and Eska 7.0 hp. An auxiliary axial flow fan was focused on the cooling fins of the engines to facilitate proper temperature control.

Engine speed was measured with an optical electronic tachometer, General Radio type 1536A, on the test tank engines.* Alternate reflecting and non-reflecting strips were painted on the flywheel. The light from the optical tachometer was reflected back to the light sensor within the tachometer. Its intensity varied according to whether the reflecting or non-reflecting surface was in the light path. Thus a pulsing signal was generated, the frequency of which was proportional to the engine speed. This device requires no physical connection to the engine. A Hewlett-Packard electronic counter was used to record and display these pulses as rpm.

---

*The 7.5 hp Mercury engine was an exception. It utilized a high voltage ignition system which caused excessive electrical noise and prevented the use of the photo pickoff system. Consequently a wire was looped around a spark plug wire and the resulting signal fed to an oscilloscope. The timed sweep of the scope was then used to determine the engine speed.

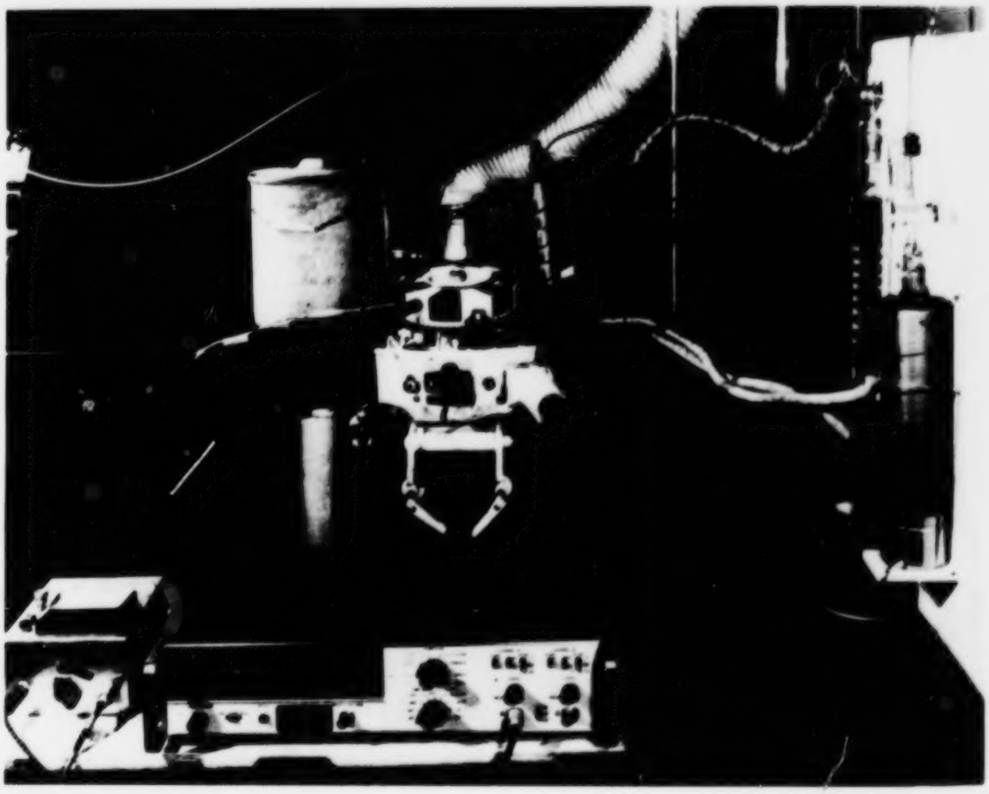

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Figure 4 Test Tank Installation Used for the Testing of the Small Engines

Drained Engines

As an addition to the original project three engines were operated with external crank-case drainage systems installed. The engines selected were similar to three of the drainless engines tested earlier, an 18 hp Evinrude, a 35 hp Chrysler, and a 50 hp Mercury. One of the engines, the 35 hp Chrysler was an older model which was normally drained. Both the 18 hp Evinrude and 50 hp Mercury were 1972 model engines which were converted from a recirculating or drainless type engine to a drained type.

The Evinrude and Mercury engines were modified to the extent that the internal recirculation line used to shunt the excess fuel and oil condensed in the crank-case back to the inlet system was removed. The port at the inlet system end was plugged. A segment of tygon tubing was connected between the internal check valve at the crank-case end and the collection apparatus. The carburetors were modified slightly to compensate for the change in mixture composition caused by elimination of drainage recirculation. The Chrysler 35 hp engine, although previously drained, required some modifications to allow collection of the drainage. An access cover was removed and the orifice used to control drainage into the exhaust leg was plugged. The drain cover was replaced with one from a later model which had an external opening.

The drainage samples were collected simply by placing a tygon tube between the drain port and a vented Erlenmeyer flask which was maintained at room temperature.

Exhaust Emission Collection and Measurement

It was not feasible to collect and analyze the total engine exhaust. Rather a representative and known fraction of the exhaust was obtained with a special sampling probe. The total sampling, condensate collection, and gas analysis systems are shown schematically in Figure 5.

The sample probes were constructed of 1/4 inch O.D. stainless steel tubing. They were designed as static probes with a number of sample holes located on the circumference and spaced longitudinally along the length of the probe. Current automotive emission testing practice was followed in the design. A typical probe is shown schematically in Figure 6.

Particular attention was directed at the location of the probe in the engine exhaust system to insure representative sampling of the average composition from all cylinders in the multi-cylinder engines and to minimize the time and spatial resolution problems. The location chosen was the position farthest down the exhaust collector, before

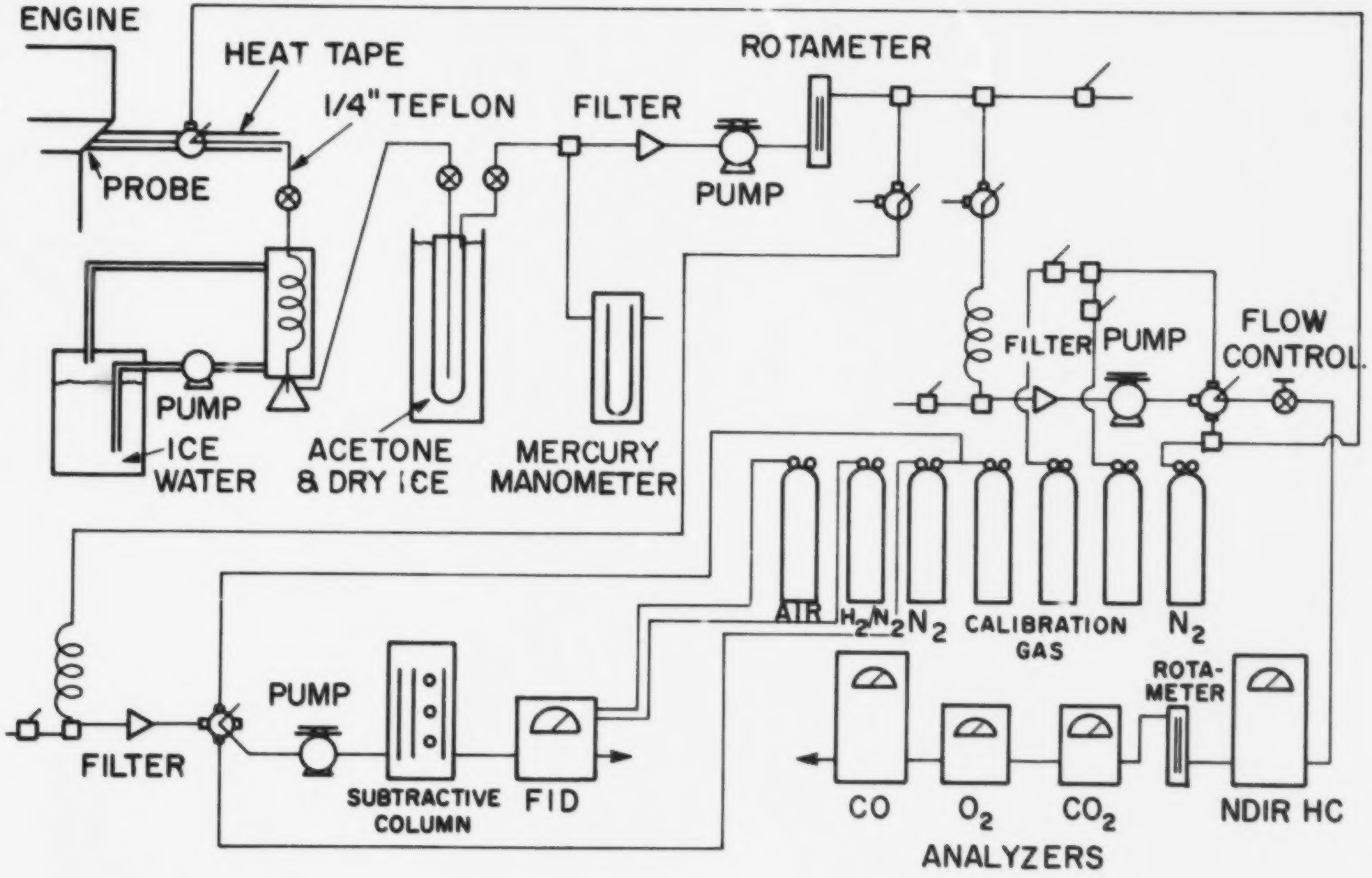
ENGINE
HEAT TAPE
PROBE
1/4" TEFLON
PUMP
ICE WATER
ACETONE & DRY ICE
FILTER
MERCURY MANOMETER
PUMP
ROTAMETER
FILTER
PUMP
FLOW CONTROL
AIR
H_2
N_2
N_2
CALIBRATION GAS
N_2
FILTER
PUMP
SUBTRACTIVE COLUMN
FID
CO
O_2
CO_2
ROTA-METER
NDIR HC
ANALYZERS

Fig. 5 Schematic Diagram of the Sample Collection and Analysis System.

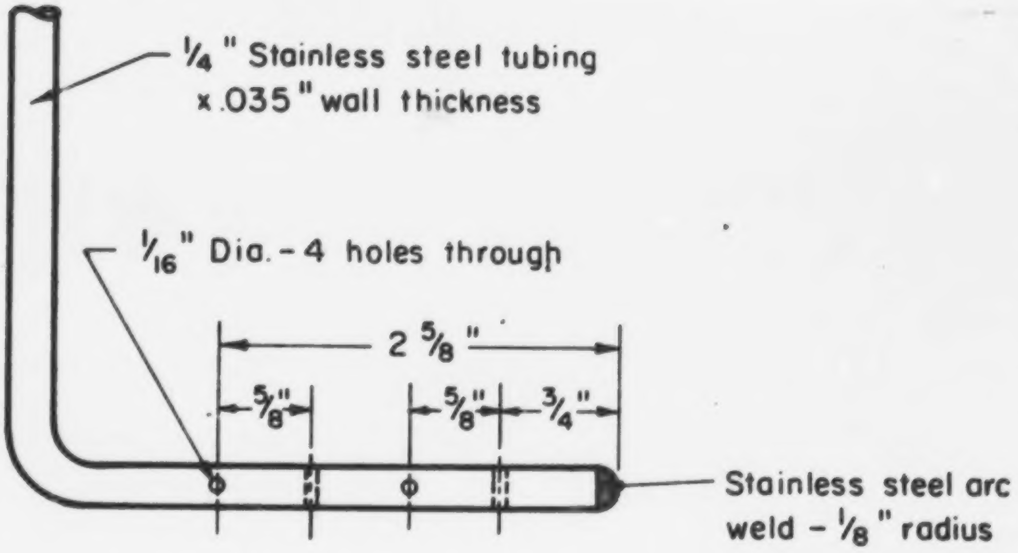
1/4" Stainless steel tubing
x.035" wall thickness
1/16" Dia.-4 holes through
2 5/8"
5/8"
5/8"
3/4"
Stainless steel arc weld - 1/8" radius

Figure 6. Exhaust Sample Probe Design

any water was added to the exhaust stream. Unfortunately the exhaust could not be collected from a large "surge" volume added to the engine exhaust system. Any such modification of the exhaust system geometry would have markedly changed engine performance.

The sample line between the engine and condensate apparatus was maintained at 350 °F. At this elevated temperature no condensation of water and only limited hydrocarbon condensation occurred on the tubing walls. Also, this temperature was still low enough to prevent significant reaction of either hydrocarbons or CO with the oxygen present.

A regulated tank of pure nitrogen was connected to a tee fitting installed in the sample line near the engine to permit a quick leak test of the sample system. Another tee was placed in the line and connected to a mercury manometer. If the manometer showed the sample line to be pressurized during a run, a leak test was unnecessary since leakage would be to the atmosphere. However, if a vacuum existed in the line, the system was checked prior to the run since room air could dilute the sample. The leak test was performed by injecting nitrogen into the sampling system at the sampling pressure. Any oxygen in the sample line as indicated by the oxygen transducer would indicate a leak.

The sample flow system allowed three separate modes of operation, Non-Dispersive-Infrared (NDIR) analyzers, Flame Ionization Detector (FID) hydrocarbon analyzers, or bypass. During the extended condensate collection runs, the system was operated in the bypass mode. Both the NDIR and FID analysis systems could be purged with room air or calibrated with span gas without affecting the flow through the condensate or liquid sample collection apparatus. A more complete discussion of the condensate apparatus is included in Part II of this report.

A viton-diaphragm, Air Shield pump was used to draw the sample through the system into a condensing coil immersed in an ice bath just before the sample was directed to the gas analysis units. This step would not normally be required in this investigation because of the prior primary and secondary condensing stages. However, several gas analysis readings were made without the initial condensation step and therefore the ice baths were always charged. Sample quenching is necessary because some of the analyzers are responsive to water and would indicate an erroneous reading if the major fraction of water vapor were not removed. The sample was also directed through a two-inch paper element filter made by Gelman Instrument Company to remove particular matter. Flow rate through the system was regulated with needle valves and measured with a Fischer and Porter rotameter.

The various emission analysis techniques used are summarized in Table 2. All of the analyzers with the exception of the hydrocarbon Flame Ionization Detector (FID) were connected in series because they are non-destructive to the sample.

Carbon monoxide (CO) was measured with an Olson-Horriba Mexa-300 Nondispersive Infrared (NDIR) analyzer. The internal pump sample was bypassed and the main system diaphragm pump was used to "push" the sample through the instrument.

Carbon dioxide (CO_2) was measured using an Olson-Horriba Mexa-200 NDIR analyzer. The internal pump was bypassed in a similar manner to the CO analyzer.

Calibration of the NDIR analyzers was performed at regular intervals using known reference or standard gas mixtures of CO and CO_2 in nitrogen (N_2). Periodic calibration of all the emission analyzers insured their accuracy. Calibration was conducted under the same sample flow conditions observed during exhaust analysis.

One of the two instruments used for hydrocarbon analysis was a Beckman Model 315 NDIR analyzer which automatically and continuously determines the concentration of a particular component of interest in a complex gas mixture. The measurement, as is the case with the Mexa-200 and 300 analyzers, is

Table 2

Gas Analysis Techniques

Exhaust Species	Technique	Make and Model	Range
Carbon Monoxide	NDIR[1]	Olson-Horiba-Mexa 300	0-10%
Carbon Dioxide	NDIR	Olson-Horiba-Mexa 200	0-15%
Hydrocarbons	NDIR	Beckman-315	500-15,000 ppm
	FID[2]	Beckman-109A	100-15,000 ppm
Oxygen	Amperometric	Beckman-715	0-21%

---

(1) NDIR - nondispersive infrared

(2) FID - Flame ionization Detector

based on a differential measurement of the absorption of infrared energy. In our study n-hexane, C_6H_{14} was selected as a model hydrocarbon. It is representative of the average composition of the unburned hydrocarbons in the exhaust gas from a gasoline engine. The unburned hydrocarbons in the two-stroke engine exhaust should have a higher average molecuulure weight than found in the four-stroke engine exhaust because more raw fuel and lubricating oil are present. However, the average composition should be relatively close to n-hexane and should cause no serious problems in interpretation of the results. It is interesting to note that over 200 different species of hydrocarbons have been identified

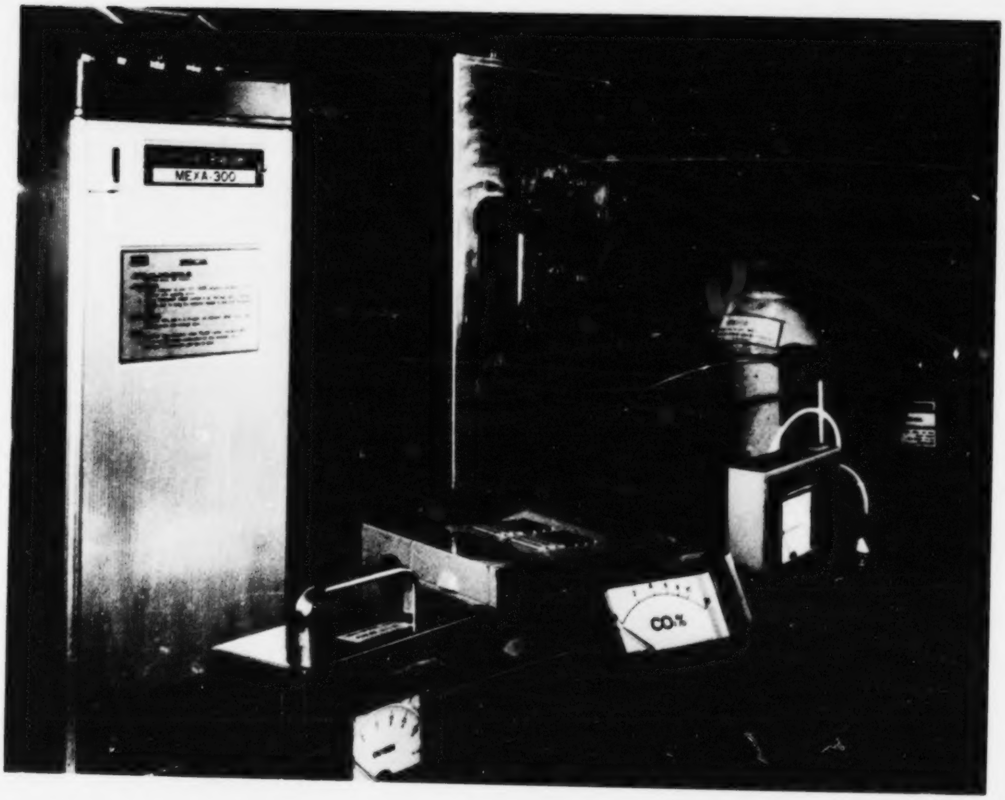

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Figure 7 Nondispersive Infrared Hydrocarbon CO, CO_2 and Amperometric O_2 Analyzers

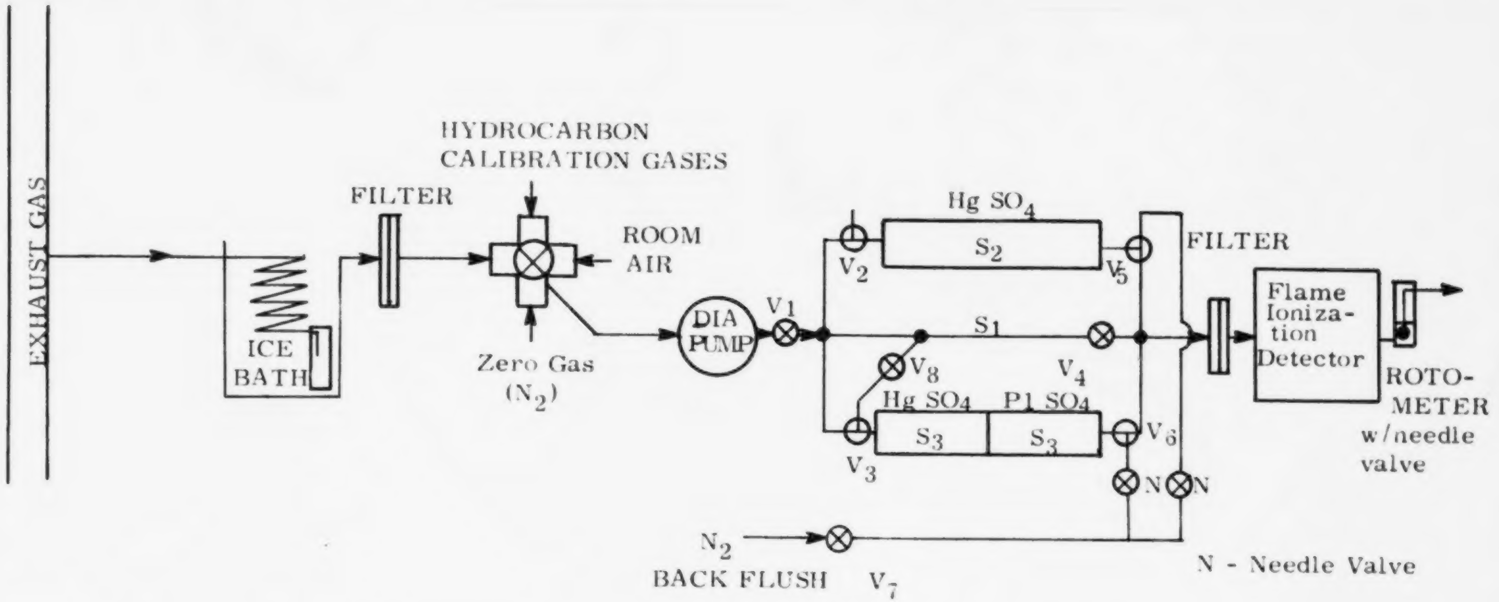
in the four-stroke engine exhaust. These range from methane (CH_4) to molecules with 10-12 carbon atoms. Significantly more compounds should be present in the outboard exhasut. The various species are distributed primarily in the paraffin, olefin, diolefin, acytelene, cyclo-paraffins, and aromatic families. Unfortunately the NDIR analyzer, sensitized to n-hexane, does not respond linearly to the carbon atoms of all species of the various families because their infrared absorption spectra only partially overlap (15). Therefore, the NDIR analyzer indicates only about one-half of the total carbon atoms that are present. A tabular presentation of the relative response characteristics of the NDIR analyzer is included in Appendix A. Therefore n-hexane or its propane equivalent (ppm hexane = 2 x ppm propane) was used as a reference gas. Initially the Beckman instrument was equipped with a 5-1/4 inch sample cell which provided accurate hydrocarbon measurement in the range from 100 to 1500 ppm. Due to consistently high hydrocarbon readings in the early testing the 5-1/4 inch sample cell was replaced with a much less sensitive 2-1/2 inch cell which permitted accurate measurement of hydrocarbon concentration in the range of 500-15,000 ppm.

The NDIR hydrocarbon, CO, CO_2 and amperometric O-analyzers are shown in Figure 7.

The second hydrocarbon analyzer used in this investigation was a Beckman Model 109A Flame Ionization Detector (FID). This unit is essentially a total hydrocarbon analyzer since it is responsive to almost all of the non-oxygenated exhaust hydrocarbons (15). Relative HC response characteristics of the FID are also discussed in Appendix A. The Beckman FID unit does possess a minor problem with O_2 interference of the HC data under certain instrument operating conditions. However, they have been modified and optimized based on prior research efforts to minimize the interference problem (16). Calibration gases used for the NDIR-HC system were also used for the FID.

A specially constructed subtractive column analyzer (17) was used in conjunction with the FID. This device permitted the separation of the gaseous hydrocarbons in the exhaust sample into principal family components: paraffins, olefins and aromatics.

A schematic diagram of the system together with a summary of its design and operating characteristics are presented in Figure 8. A photograph of the system is shown in Figure 9.


EXHAUST GAS
ICE BATH
FILTER
HYDROCARBON CALIBRATION GASES
ROOM AIR
Zero Gas (N2)
DIA PUMP
V1
V2
Hg SO4
S2
V5
FILTER
S1
V8
V4
Hg SO4
Pd SO4
S3
S3
V3
V6
N
N
Flame Ionization Detector
ROTO-METER w/needle valve
N2
BACK FLUSH
V7
N - Needle Valve

				Operation of Valves				
Position	Sample Seen by FID	Flow Path	Scrubber	$V_{7,8}$	V_1	$V_{2,5}$	$V_{3,6}$	V_4
1	Back flush	S_2S_3	All	On	Off	Off	Off	On
2	Paraffins and benzene	S_3	$HgSO_4$ and Pd	Off	On	Off	On	Off
3	Total olefins	S_2	$HgSO_4$	Off	On	On	Off	Off
4	Total or zero	S_1	None	Off	On	Off	Off	On

Figure 8. Flow Schematic of the University of Michigan Subtractive Flame Ionization Hydrocarbon Analysis System

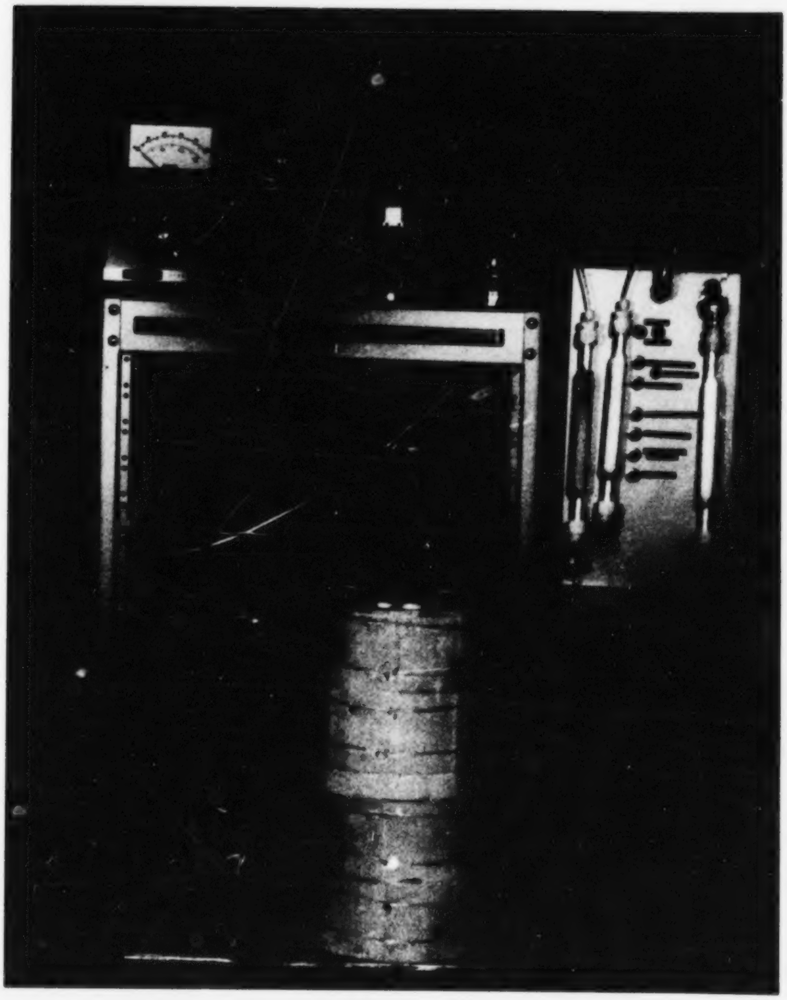


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Figure 9 Front View of the Subtractive Column Flame Ionization Hydrocarbon Analysis System

The subtractive column has four modes of operation. Mode 1 backflushes all three scrubbers with nitrogen. Mode 2 directs the sample through a mercuric sulfate prescrubber to remove the olefinic fraction and then through a palladium sulfate-sulfuric acid scrubber to remove the aromatic fraction. The indicated hydrocarbon concentration is then the paraffinic hydrocarbon concentration. In mode 3 the sample is passed through a mercuric sulfate scrubber to remove the olefinic fraction. The FID reading is now the concentration of both paraffinic and aromatics. Mode 4 passes the sample directly to the FID for a total hydrocarbon concentration value. The olefinic and aromatic fractions are obtained simply by a differencing technique. An additional discussion of the subtractive column technique is included in Appendix A.

Test Procedures

Prior to data acquisition, all of the engines were broken in according to the manufacturer's recommendations.

Idolene 30* was used as the test fuel. All of the fuel used was from the same refinery batch, thus insuring consistent hydrocarbon family composition. Indolene is a specially blended fuel that is representative of the average composition of gasoline. Pertinent characteristics of the fuel are indicated in Appendix A. Quicksilver Outboard motor oil was used as the lubricant in all of the engines. It was mixed with the fuel in the ratio specified by each manufacturer.

---

*Indolene fuels are used for all automotive emission testing.

The engines were run only under steady-state conditions. With the dynamometer speed and load could be controlled. Therefore a simulated boat-load curve was used to establish the proper speed-horsepower relationship. Generally an outboard engine follows approximately a 2.5 order load curve on a planing hull. A sample curve for a 100 hp engine is shown in Figure 10.

Unfortunately the speed load relationship of the engines run in the test tank was primarily a function of the test prop design. However, testing by the various manufacturers has shown that the load characteristic is representative of a true boat load curve. Of course it must be recognized that there are practically an infinite number of boat-load curves. The particular curve is a function of the hull and prop design, magnitude and distribution of load in the hull, water conditions and type of use. An engine-operated on any boat-load curve within this range should exhibit similar emission performance, however.

The test runs were of two basic types: condensate

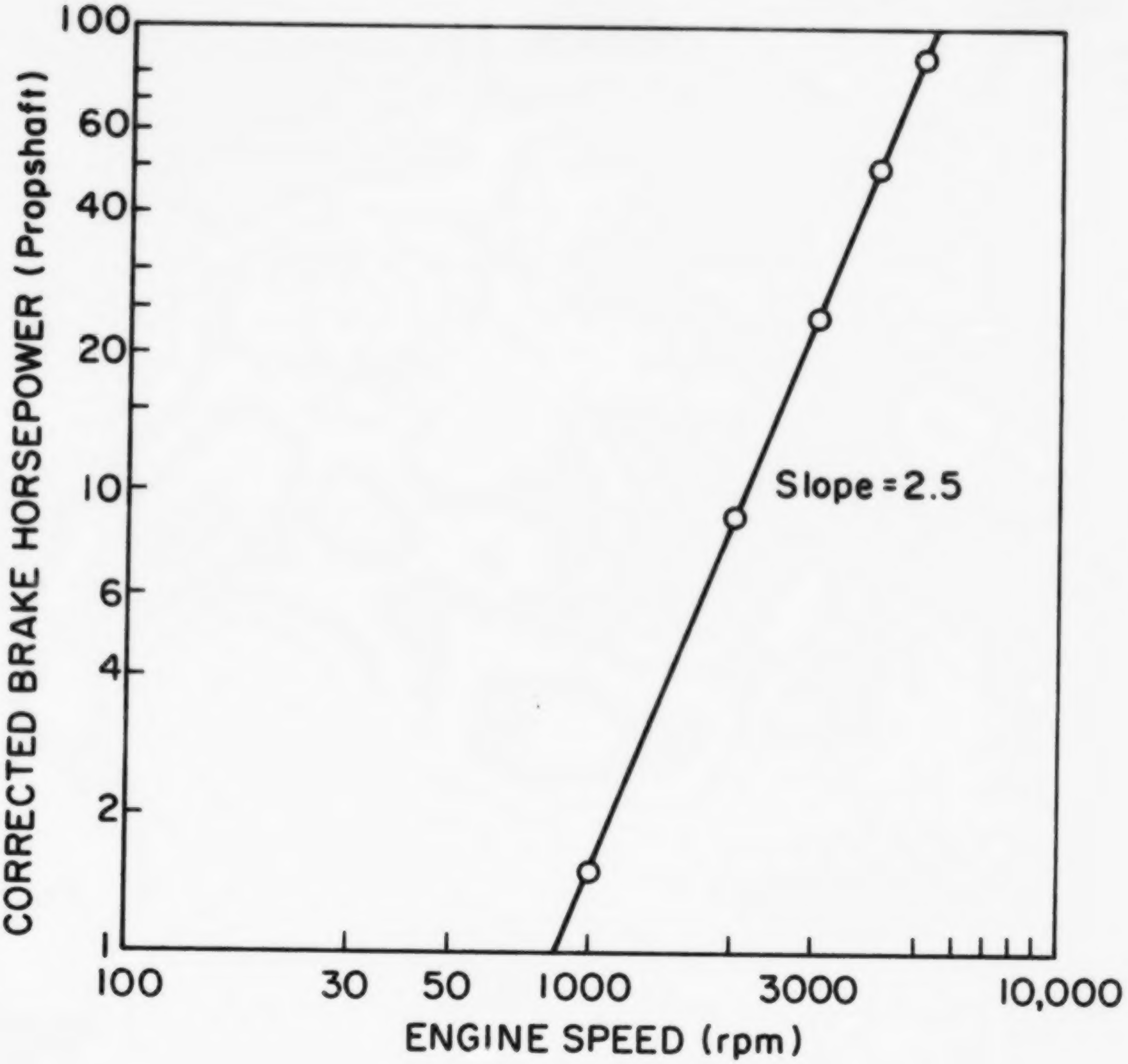


Figure 10 Representative Boatload Curve.

collection and gaseous exhaust analysis.

Collection of condensate samples required 3 hours of continuous operation. During these runs the gaseous exhaust products were monitored at 1/2 hour intervals. Only the various NDIR and O_2 analyzers were used for this check on engine performance.

The normal gaseous exhaust analysis tests were conducted without the condensate collection apparatus in the sample line. During these runs, all of the gas analysis equipment was used, although the NDIR and FID analyses could not be made concurrently, Incidentally, only insignificant differences were observed between the emissions measured with and without the low temperature condensors in operation. This was expected since only a small fraction of the unburned hydrocarbons were condensable.

Tests on the special engines with crank-case drainage were conducted in a similar fashion to the drainless engines. However, a drainage sample was collected for analysis by the Water Resources Laboratory.

The final engine tests on this project were the emission evaluation of the Chrysler 35 hp and Evinrude 18 hp supplied by ENCOTEC. Tests were conducted prior to and after normal maintenance procedures were applied to the engines. Tune-up consisted of a general engine clean-up, replacement of spark plugs and carburetor inspection. The actual testing was conducted in a manner similar to all prior testing including condensate acquisition and gas analysis.

RESULTS AND DISCUSSION

A substantial quantity of data was accumulated during the test program. This discussion is directed principally at a presentation of results rather than an engineering analysis of these results.

Gaseous Exhaust Emissions

Numerous exhaust constituents were measured including CO, CO_2, O_2 and NDIR and FID hydrocarbons. Not all of these are toxic to aquatic organisms, nor are those toxic constituents of equal toxicity. It was deemed advisable, however, to measure all principal components to aid our understanding of the emission formation processes in two-cycle marine engines.

Carbon Monoxide

Carbon monoxide is moderately toxic to many air breathers and has limited solubility in water. Therefore, most of the engine exhaust CO would be considered an air pollutant. The CO concentration is summarized in Table 3 for all the test

ENGINE	RPM						
	1000	1500	2000	3000	4000	4500	5000
CHRYSLER 3.6	5.35		6.35	5.90	3.75	3.80	
EVINRUDE 6.0	1.75		5.25	6.25	3.10		
ESKA 7.0	2.95		5.35	8.14	8.10		7.80
MERCURY 7.5	4.80	4.70	5.20	1.95	1.20		
CHRYSLER 12.9		5.35	5.27	5.06	5.06	4.80	4.40
EVINRUDE 18.0	5.00	5.65	5.45	7.55	7.10		
EVINRUDE 18.0*	4.89	5.25	4.76	6.84	5.55	5.70	
CHRYSLER 35		6.21	5.21	8.45	3.92		
CHRYSLER 35*	6.50	6.94	7.69	9.52	5.11		
MERCURY 50	4.80	3.90	3.26	5.26	4.26		
CHRYSLER 105	4.57	3.93	3.12	3.82	3.57		
AVERAGE	4.51	5.24	5.17	6.25	4.61	4.77	6.10

* Maintenance study field engines

Table 3 CO Concentration-Percent vs. rpm for "Drainless Outboard Engines

engines. Note that the two tuned engines from the maintenance influence study are included. The average carbon monoxide emissions are plotted in Figure 11 as a function of engine speed. The results have not been plotted at 4500 and 5000 rpm on the "average" curve in Figure 11 because data at this speed were taken from only a few engines. Carbon monoxide emission results are plotted for all the engines in Appendix A in Figures 1 through 9 and in Figures 26 and 27 in the text (tuned engines). No trend is evident in the plot of the average results. The CO emissions are high compared to those observed from current four-cycle automotive engines.

Carbon monoxide is basically a function of the engine air-fuel ratio. A generalized set of curves showing various major exhaust constituents as a function of air-fuel ratio is shown in Figure 12. This clearly suggests that the high CO emissions of the two-cycle marine engines are a result of a rich mixture ratio. The air fuel ratio used on all of the test engines was richer than the stoichiometric ratio of approximately 14.8 to 1. Generally the air-fuel ratio used was between 10 and 13 to 1. This is far richer than normally encountered in a typical automotive four-cycle engine under steady-state operating conditions. This richness is necessary to assist with internal cooling and lubrication, and provide smooth operation even with substantial internal exhaust

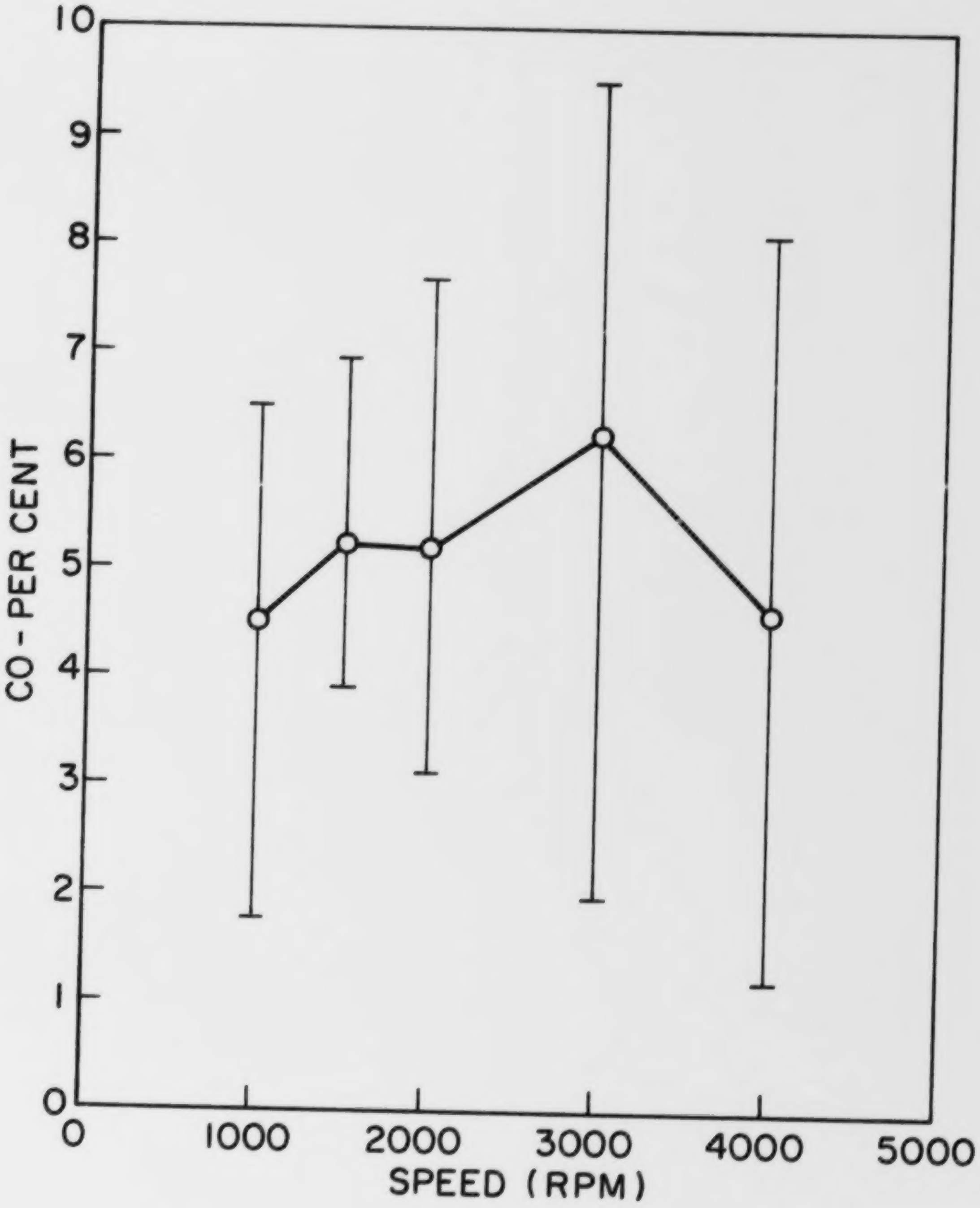


Figure 11 Summary of Carbon Monoxide Concentration Emissions at the Boat-Load Test Conditions for 11 "drainless" Engines.

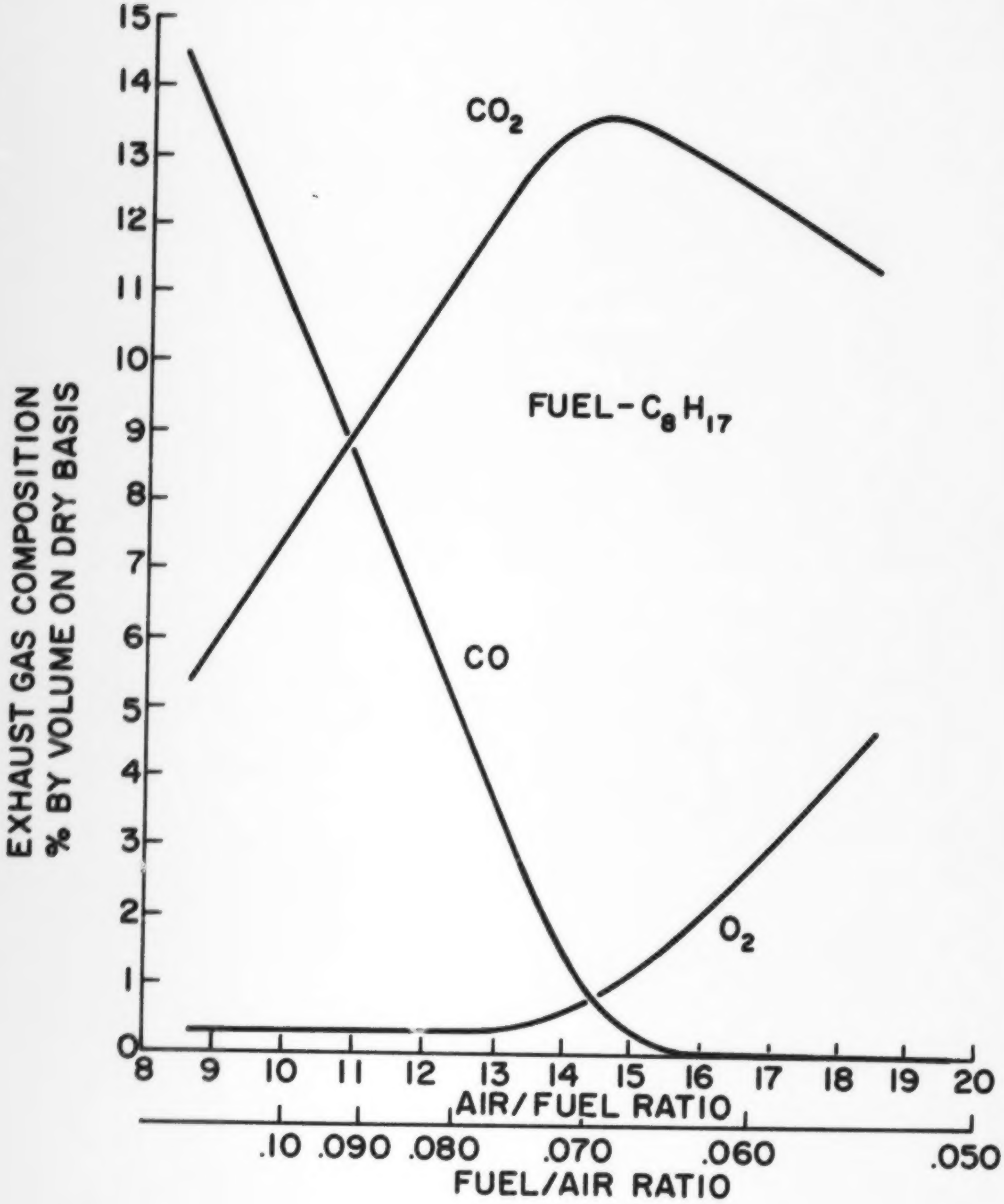


Figure 12 Exhaust Gas Composition as a Function of Air-Fuel Ratio for a Typical Hydrocarbon Fuel.

residual dilution which is a problem of all two-cycle, crankcase scavenged engines.

Another factor influencing the carbon monoxide emissions is the trapping efficiency of the engine which is defined as the ratio of the mass of fuel and air trapped in the engine to that which is furnished to the engine. The lower the trapping efficiency, the greater the quantity of unburned fuel and air in the exhaust and therefore, for a given mixture ratio, the lower the CO emissions. The unburned fuel/air in essence dilutes the exhaust products. Trapping efficiency will be discussed in a later section.

The spread of CO data from one engine to another at a given test condition was very broad as indicated in Figure 11. The primary reason for this variation is the wide range of air-fuel ratios used in the engines. Air-fuel ratio is set at the factory in the case of fixed jet carburetors or by the operator in the case of variable jet carburetors. The setting is chosen to optimize the engine's performance. Because these engines are often significantly different from one another in design, the mixture ratio for best performance is highly variable and therefore the carbon monoxide emission results are variable from engine to engine.

Carbon Dioxide --

Carbon dioxide is not considered a pollutant in normal atmospheric concentrations; however, it is a very significant constituent in gasoline engine exhaust. The data from the various test engines is summarized in Table 4, and the average results of these engines is plotted in Figure 13. The CO_2 results from all engines is plotted in Figures 1 to 9 in Appendix A and in Figures 26 and 27 in the text (tuned engines). As with CO, the concentration of CO_2 is strongly a function of the mixture ratio used in the engine, Figure 12. In addition, trapping efficiency also influences CO_2 concentration. In general the CO_2 concentration should be inversely proportional to the carbon monoxide concentration, although this is not evident in comparing Figures 11 and 13. There are two factors that cause deviation from the expected behavior: 1) trapping efficiency increases with engine speed resulting in an increase in both CO and CO_2, and 2) the averaging process used to generate the curves from the individual engine data hides the emission performance of individual engines.

Hydrocarbon Emissions --

Unburned hydrocarbons are considered to be a major pollutant. However, not all of the individual hydrocarbons are equally toxic to aquatic life. By comparison, in a typical automotive (four-stroke) engine exhause more than 200 different species of hydrocarbons have been identified. Some, such as methane are relatively non-toxic, and others such as

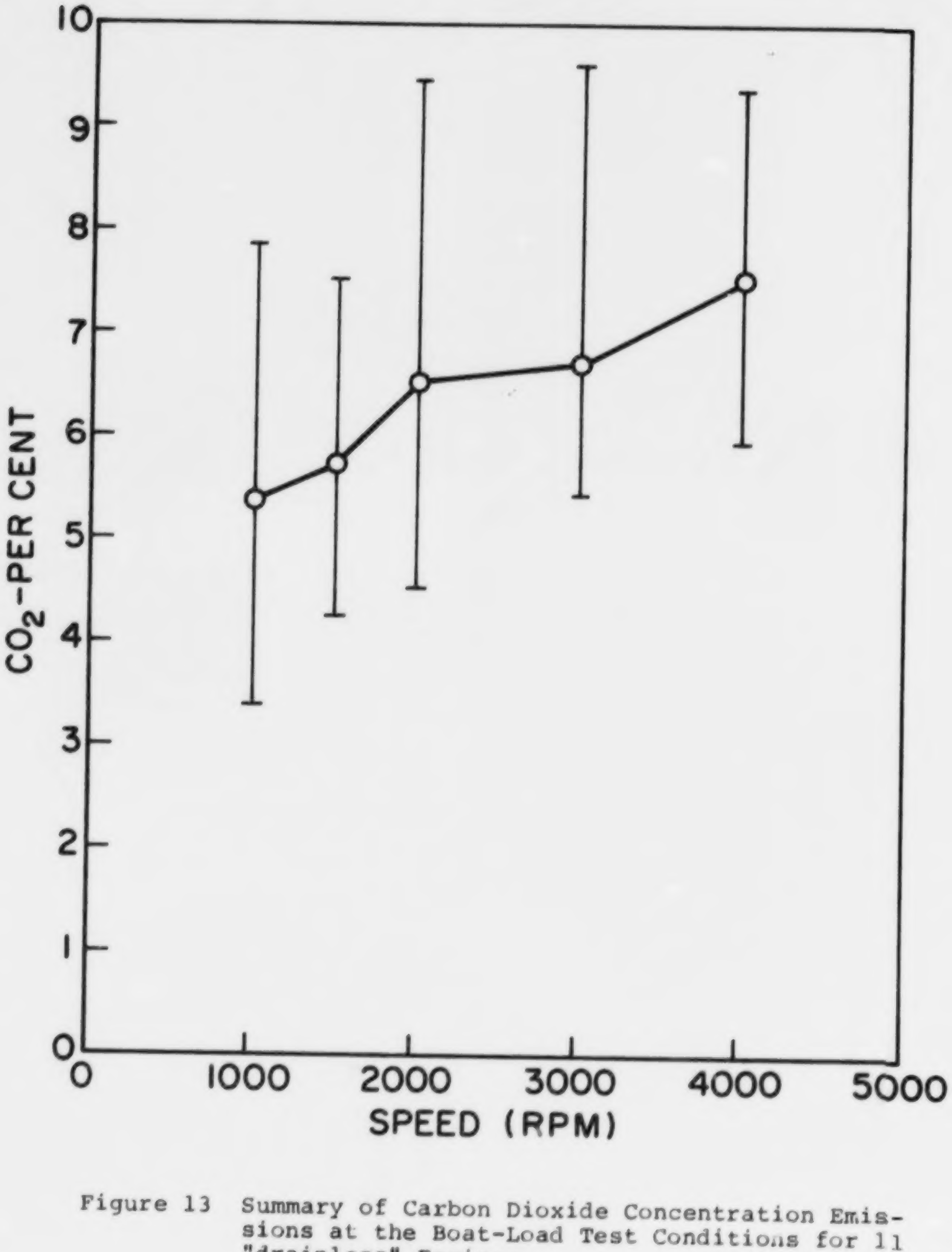


Figure 13 Summary of Carbon Dioxide Concentration Emissions at the Boat-Load Test Conditions for 11 "drainless" Engines.

CO_2 CONCENTRATION-PERCENT

ENGINE	RPM						
	1000	1500	2000	3000	4000	4500	5000
CHRYSLER 3.6	4.20		4.55	6.45	8.10	7.75	
EVINRUDE 6.0	7.15		5.55	5.60	7.45		
ESKA 7.0	7.85		5.95	5.65	6.10		5.80
MERCURY 7.5	6.05	6.90	7.00	9.14	8.85		
CHRYSLER 12.9		4.25	5.00	6.49	6.36	5.80	6.40
EVINRUDE 18.0	3.40	4.80	6.50	6.90	5.95		
EVINRUDE 18.0*	3.42	4.09	5.77	6.09	7.05	6.86	
CHRYSLER 35		6.12	7.63	5.45	8.49		
CHRYSLER 35*	5.30	6.14	7.13	5.60	7.31		
MERCURY 50	4.70	5.96	7.43	6.96	7.96		
CHRYSLER 105	6.27	7.53	9.47	9.59	9.39		
AVERAGE	5.37	5.72	6.54	6.72	7.54	6.33	6.10

* Maintenance study field engines

Table 4 CO_2 Concentration-Percent vs. rpm for "drainless" Outboard Engines.

propylene can have a more significant environmental impact. The hydrocarbon measurements were an important part of this study, particularly since they were considered to be the major collection of compounds of concern as water pollutants. Only the flame ionization detector (FID) hydrocarbons will be discussed since this number is representative of the total hydrocarbon concentration rather than the partial hydrocarbon fraction shown by the non-dispersive infrared (NDIR) analyzer. The total hydrocarbon results at the various test speeds are summarized in Table 5. The average hydrocarbon data from all test engines at each speed is plotted in Figure 14, except for the 4500 and 5000 rpm test conditions where limited data was obtained. Both the NDIR and FID hydrocarbon data are plotted in Figures 10 through 18 in Appendix A and Figures 28 and 29 of the text (tuned engines). All hydrocarbon data is expressed as ppm of n-hexane, C_6H_{14}.

The total hydrocarbon emissions are higher than those observed from a typical four-cycle gasoline engine by at least a factor of 10. This is partially due to the richer mixture ratios used in the two-cycle engine, but more significantly it is related to the trapping efficiency. If the mixture is not trapped within the engine cylinder, it is over-scavenged or in effect "dumped into the exhaust system before it has an opportunity to burn. The concentration of

CONCENTRATION-PPM

FID-HYDROCARBONS

ENGINE	RPM						
	1000	1500	2000	3000	4000	4500	5000
CHRYSLER 3.6	10000		9300	6500	5600	4550	
EVINRUDE 6.0	5400		7300	7000	7200		
ESKA 7.0	7500		9100	7200	6900		6700
MERCURY 7.5	7700	5900	5600	4900	4600		
CHRYSLER 12.9		9200	7800	6400	6500		6800
EVINRUDE 18.0	8600	7350	6100	6700	7200		
EVINRUDE 18.0*		10987	8042	6483	5850	5918	
CHRYSLER 35		5850	4500	5375	4525		
CHRYSLER 35*	6800	6775	4750	5250	4550		
MERCURY 50	8200	7850	6150	5700	4550		
CHRYSLER 105	7800		5250	4650	4550		
AVERAGE	7750	7701	6717	6014	5638	5234	6750

* Maintenance study field engines

Table 5 Concentration-ppm FID-Hydrocarbons vs. rpm for "drainless" Outboard Engines.

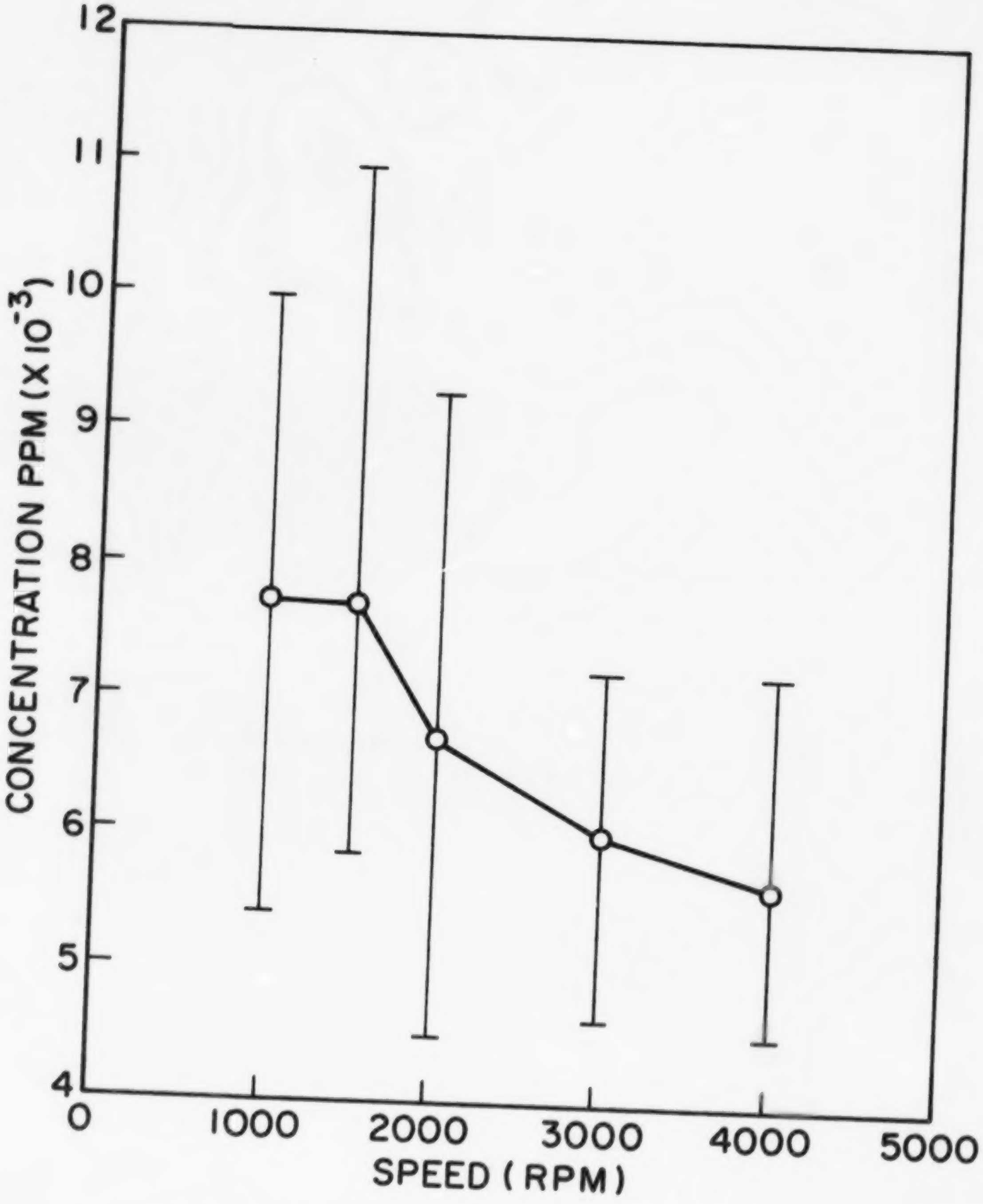


Figure 14 Summary of Total Hydrocarbon Concentration Emissions at the Boat-Load Test Conditions for 11 "drainless" Engines.

hydrocarbons in the unburned mixture is extremely high, 20,000 ppm of C_6H_{14}. Therefore, even a small fraction of lost mixture can contribute significantly to the total hydrocarbon emission level. In general, the hydrocarbon emissions tend to decrease with increasing speed. This result is consistent with both the decreasing fuel-air ratio and the improved trapping efficiency observed as the speed increases.

A moderate spread of total hydrocarbon emissions was observed at each speed from one engine to another. For example, at 2000 rpm the spread was from 4500 ppm to 9300 ppm. It should be noted, however, that the percentage spread was far less than observed with the carbon monoxide emissions.

Trapping Efficiency

Trapping efficiency is a very improtant measure of the engine's ability to retain the fuel and air that is furnished to the engine. Ideally this should be 100%; however, with the dynamic scavenging used with current small two-cycle engines this goal is essentially impossible to achieve. Trapping efficiency or perhaps a better term would be pseudo-trapping efficiency can be obtained from analysis of exhaust oxygen concentration. With normal rich mixture combustion we would expect only a very small exhaust O_2 concentration, perhaps one or two-tenths of a percent. The O_2 found in two-cycle exhaust (with rich fuel and air mixtures delivered by the carburetor) is primarily related to the fuel and air that is not burned either because of over-scavenging or incomplete combustion within the combustion chamber. The concept of pseudo-trapping efficiency recognizes that all unburned mixture may not be due to over-scavenging. If we observed 21% O_2 in the exhaust gas, this would suggest that combustion was not taking place in the engine and would in effect result in zero trapping efficiency. On the other hand, zero percent oxygen in the exhaust represents a condition where all the mixture was burned and would mean the engine had a trapping efficiency of 100%.

Trapping efficiency is particularly important from the standpoint of engine fuel consumption and hydrocarbon emissions as discussed in the previous section. All of the engine trapping efficiency data is summarized in Table 6 and the average data from the test group at each test condition are plotted in Figure 15. Trapping efficiency is plotted as a function of speed for each engine in Appendix A, Figures 10 to 18 and in Figures 28 and 29 in the text. In general, trapping efficiency increases with speed and appears to reach a maximum in the vicinity of 3000 to 4000 rpm. Again a

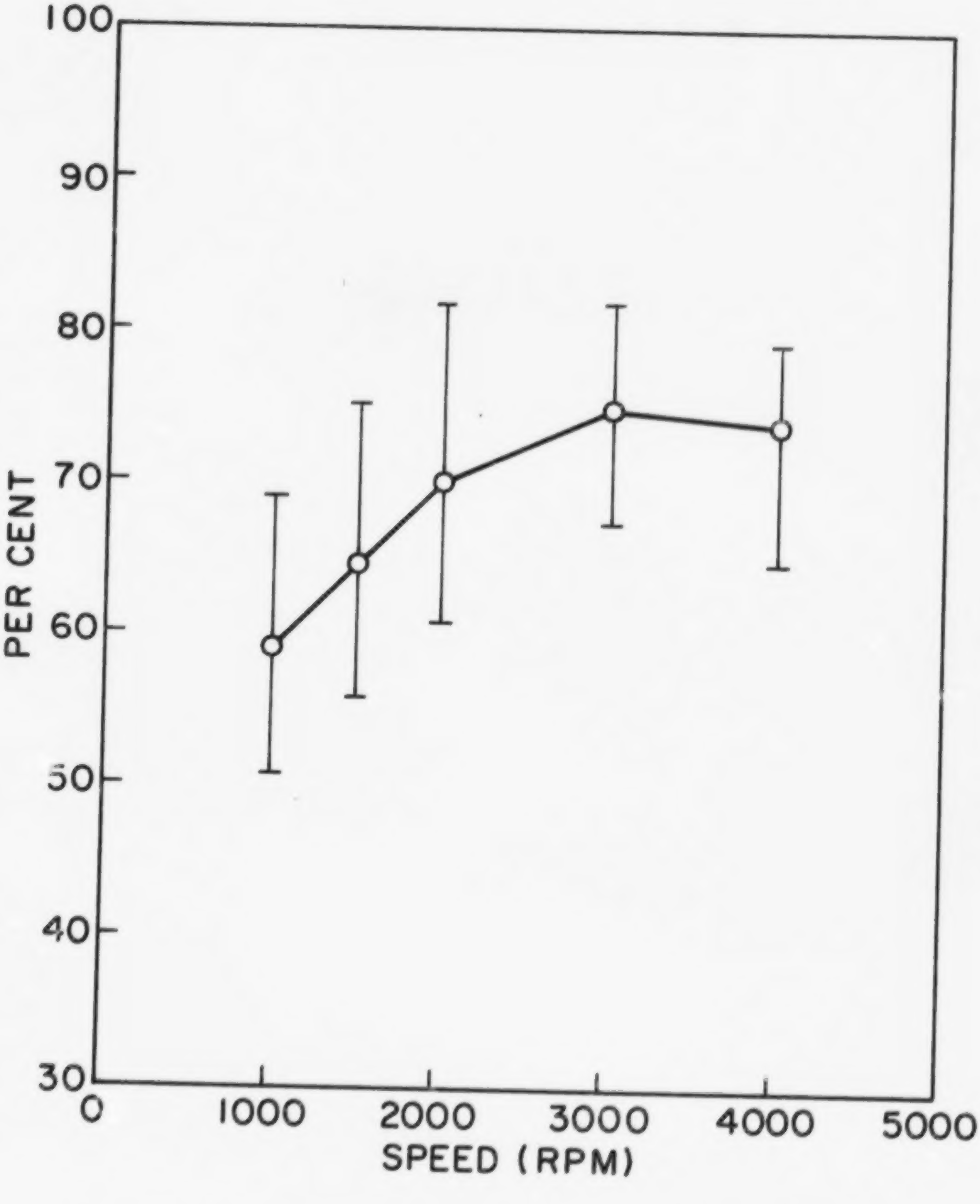


Figure 15 Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions for 11 "drainless" Engines.

TRAPPING EFFICIENCY-PERCENT

ENGINE	RPM						
	1000	1500	2000	3000	4000	4500	5000
CHRYSLER 3.6	57.2	62.9	72.7	76.0	74.4		
EVINRUDE 6.0	53.1		63.4	67.2	64.6		
ESKA 7.0	63.6		65.3	75.1	77.0		71.7
MERCURY 7.5	62.9	62.2	73.9	72.2	69.4		
CHRYSLER 12.9		55.7	60.6	69.4	67.5	65.5	65.0
EVINRUDE 18.0	52.2	60.3	69.4	76.1	73.4		
EVINRUDE 18.0*	50.5	57.0	66.7	75.7	76.6	75.6	
CHRYSLER 35		75.1	78.4	76.7	75.4		
CHRYSLER 35*	68.9	73.9	81.7	80.9	76.4		
MERCURY 50	56.5	61.2	68.4	73.8	75.8		
CHRYSLER 105	64.2	70.2	78.1	81.8	79.1		
AVERAGE	58.8	64.5	69.9	74.7	73.7	71.9	68.4

* Maintenance study field engines

Table 6 Trapping Efficiency-Percent vs. rpm for "drainless" Outboard Engines

moderate spread is observed between engines. Several of the engines exhibit a trapping efficiency exceeding 80%; others, particularly at the low load and speed test conditions, may lose nearly half of the unburned mixture to the exhaust with a consequent high level of hydrocarbon emissions.

Again it should be noted that the emission data used to compile Tables 4, 5 and 6 included the results from the "tuned" engines studied in the last phase of the program. Therefore the results are shown for two Evinrude 18 hp engines and two Chrysler 35 hp engines. Both of these engines used fixed high speed carburetor jets. A point of interest concerns the relative emission performance of this pair of engines. The results showed that the two 18 hp Evinrude engines were very similar to one another and likewise the two 35 hp Chrysler engines were remarkably similar to one another with respect to emission performance. Clearly this suggests that the quality control of the manufacturers is excellent, although the limited sample prevents us from drawing such a specific conclusion.

Mass Emission Results --

The previous discussion focused on the concentration emission characteristics of the various test engines. Of ultimate concern, however, are the mass rate of undesirable emissions which enter the atmosphere. This quantity is the

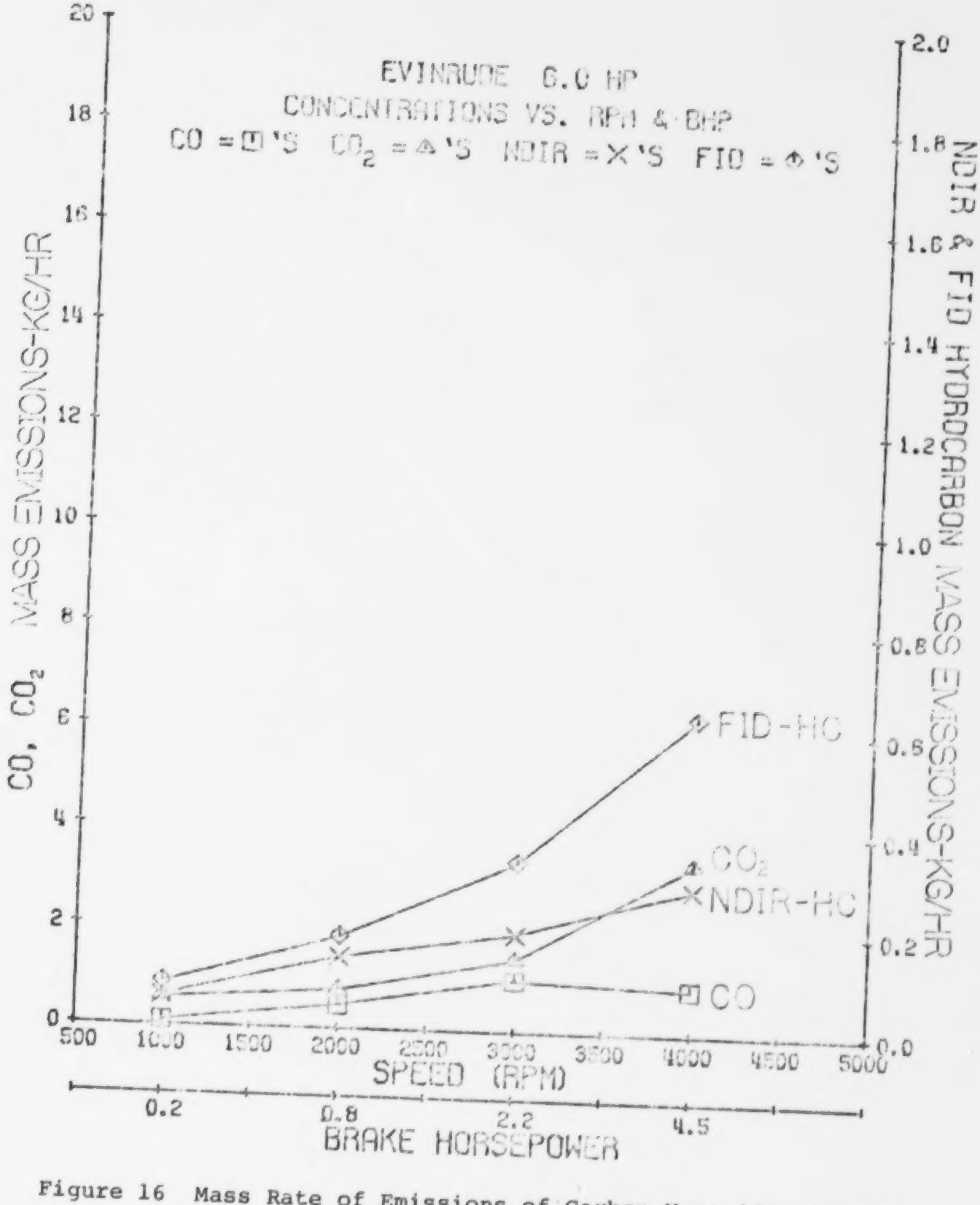


Figure 16 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 6 hp Evinrude Engine

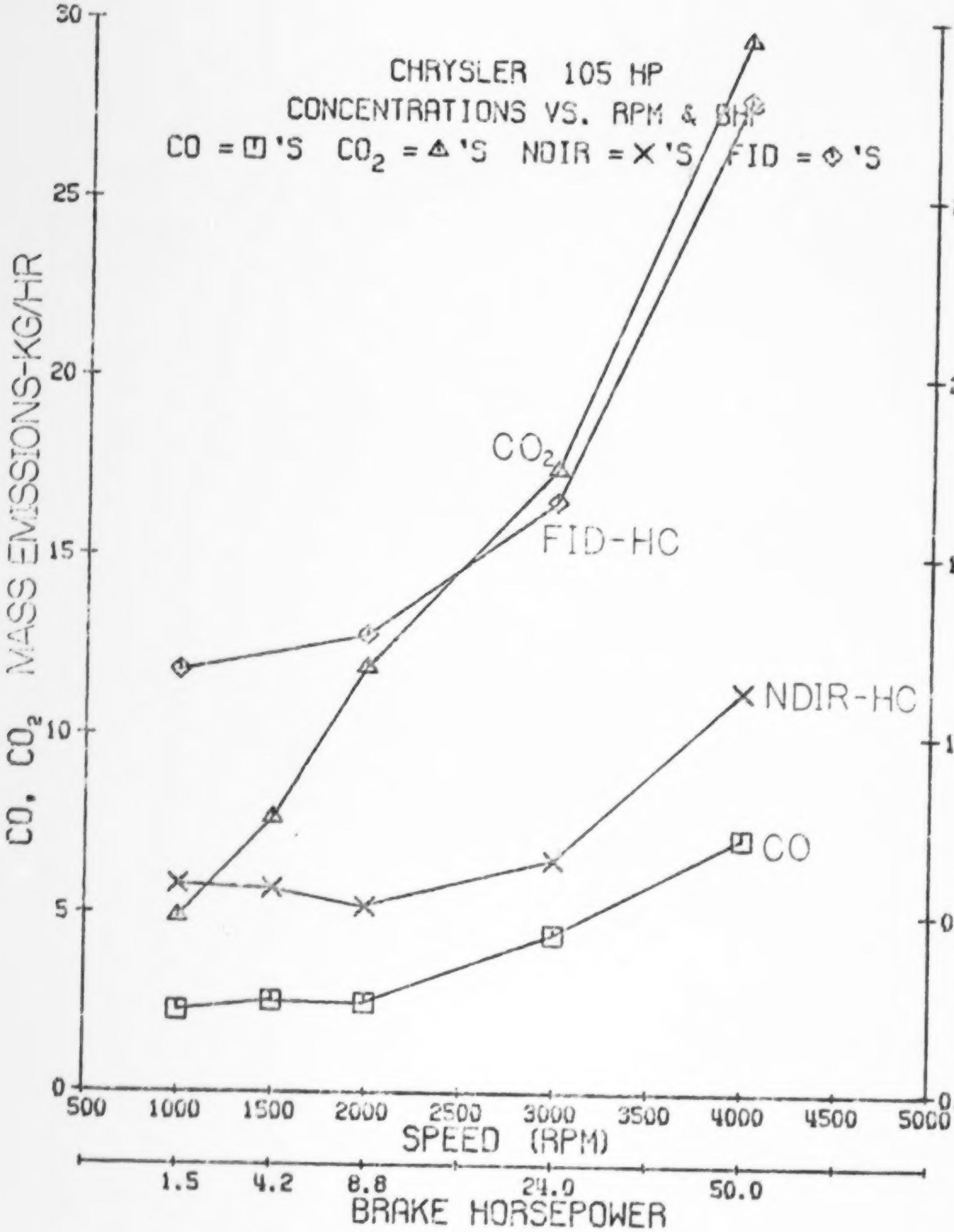


Figure 17 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 105 hp Chrysler Engine

product of the concentration emissions and a mass flow factor related to the flow rate of air and fuel required by the engine to satisfy a given speed and load requirement. Results from the largest engines tested -- 105 hp Chrysler and one of the smaller engines -- a 6 hp Evinrude are plotted in Figures 16 and 17 to illustrate the nature of the results. Since the concentration emissions from this pair of engines are similar, the major factor causing the much higher mass emissions from large engines is the greater air and fuel flow rate. Brake horsepower is also plotted on the abscissa of these curves and is closely related to the mass flow rate. In general the mass rate of emissions increased with speed and horsepower for each of the engines. Mass emission data from the additional engines are included in Figures 19 through 25 in Appendix A and Figures 30 and 31 of the text.

Hydrocarbon Family Analysis

The exhaust hydrocarbons were separated into their primary family constituents (paraffins, aromatics and olefine) with the aid of the subtractive column analyzer.

Sample results from two engines, the 105 hp Chrysler and 6 hp Evinrude are presented in Figures 18 and 19. Results from the rest of the engines are shown in Appendix A, Figures 26 through 32, and in Figures 32 and 33 of the text the various constituents are shown on a cumulative scale. In general the results differ significantly from those observed with the conventional four-cycle engines in that the exhaust hydrocarbons appear to be more closely related to the fuel. The major differences observed between the exhaust hydrocarbons and the fuel was the olefin concentration which is moderately greater in the exhaust gas, averaging between 20% and 30% of the total hydrocarbon composition, whereas in the fuel the olefin fraction was 6%. The increase in olefins is a result of "restructuring" primarily of the paraffinic hydrocarbons during the combustion process. Most of this reaction occurs in a "quench zone" which is located between the hot flame and the relatively cold walls of the engine combustion chamber.

The aromatic fraction is slightly less than observed in the fuel and is generally in the range of 20-30% of the total hydrocarbon composition. As a class, the aromatics appear to be relatively stable.

The paraffinic hydrocarbons generally are the most prevalent of the exhaust hydrocarbons and comprise approximately 50% of the total. However, in some instances the paraffinic fraction, such as with the 6 hp Evinrude engine, was nearly 70% of the total and very similar to the fraction of paraffins observed in the test fuel. Other engines, such as the 3.6 hp Chrysler, exhibited only approximately 45% paraffinic hydrocarbons under several test conditions.

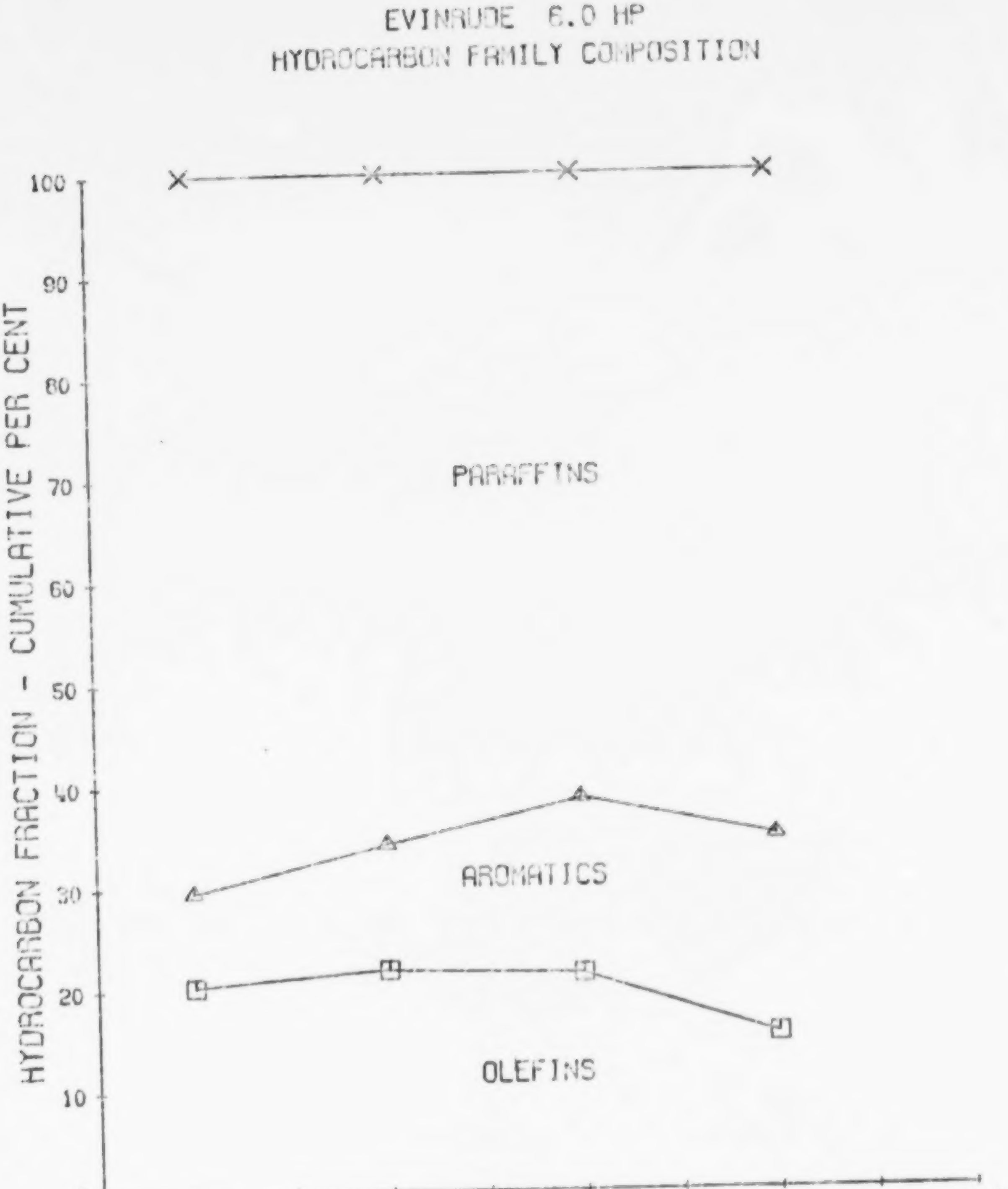


Figure 18 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 6 hp Evinrude Engine

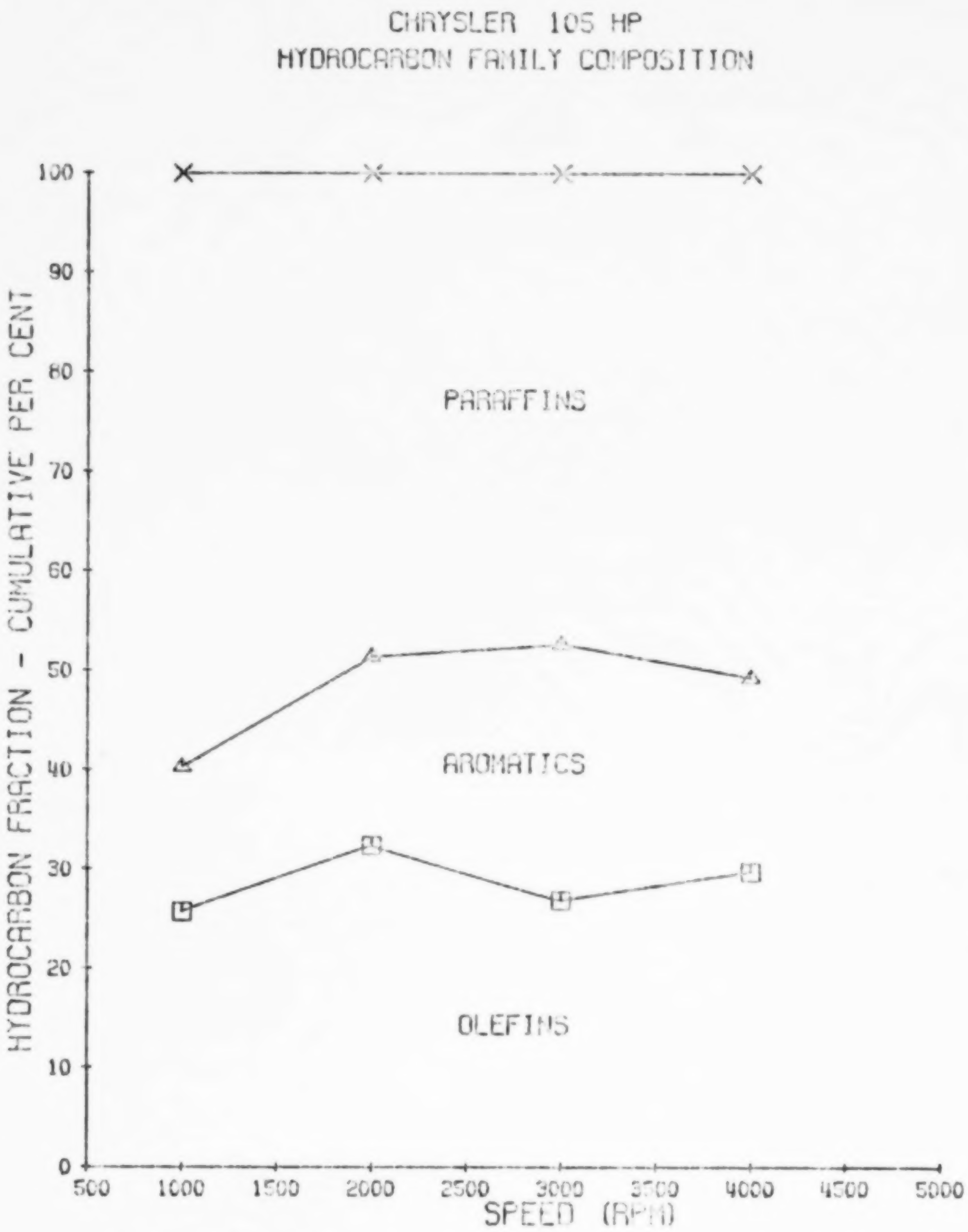


Figure 19 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 105 hp Chrysler Engine

No discernible trend is evident with regard to the hydrocarbon family breakdown as a function of engine speed and load.

Studies of Crank Case Drainage

Three engines were investigated with internal crank-case drainage rather than the recycling system used on all current engines. The engines selected were the 35 hp Chrysler, 50 hp Mercury and 18 hp Evinrude. Drainage is stated as a rate in grams per hour, and as the percentage of fuel used by the engine. The averaged results are plotted in Figures 20 and 21 from data in Table 7.

A relatively wide variation was observed between the three test engines. The Chrysler in particular exhibited substantial drainage at the low speed test conditions. However, as with all of the engines, the drainage tended to decrease with an increase in engine speed. Decreased drainage with increasing speed was expected because the greater air flow at higher speed results in more crank-case turbulence. The greater turbulence tends to carry the oil and heavier fuel molecules into the engine cylinder rather than permitting them to accumulate in the crank-case. No explanation is evident for the drainage differences observed between the engines other than it is related to the particular design characteristics of the engine.

A maximum drainage rate of approximately 300 grams per hour was observed at the 1500 rpm test condition with the

Chrysler and a minimum rate of less than 40 grams per hour at 4000 rpm with the 18 hp Evinrude engines. In terms of the percentage of fuel used, the drainage observed ranged from 11% at 1000 rpm for the Chrysler engine to less than 1% for the Mercury 50 hp engine at the 3000 rpm test condition. At low speed substantial variation was observed in the results from run to run for a given engine. For example, with the Mercury 50 hp engine at 1500 rpm a drainage rate of 179.0 gms/hr was observed as the speed was increased to the test speed, whereas a drainage rate of 3.7 gms/hr was observed when the speed was decreased to this test speed. This suggests that a hystersis effect is present such that if one would approach a given speed from one side we would expect to see a different crank-case drainage than if one approached the speed from the other side. This is probably related to the slight differences in combinations of spark advance and throttle settings required to maintain a given performance level. This difference is amplified by the steep slope of the drainage curve evident in the low speed range of the engine.

The oil content of the drainage samples was calculated in two ways. In the first, the boiling range composition of the sample was measured. Since more than 90% of the oil components boil higher than any gasoline component, it was possible to estimate oil content from this data. A second

Table 7 Crank Case Drainage

Mercury 50 HP - Drained

RPM	DRAINAGE g/hr.	DRAINAGE - % FUEL
1500	3.7	.10
	197	6.31
2000	106	2.8
	7.9	.20
	6.5	.18
3000	58.4	.86
	54.3	.79
	8.2	.12
4000	--	--

Chrysler 35 HP - Drained

RPM	DRAINAGE g/hr.	DRAINAGE - % FUEL
1000	215	8.81
	314	13.27
1500	328	9.24
	249	7.24
2000	124.7	3.11
	146	3.61
3000	34.7	.54
	44.7	.71
	51.0	.81
4000	82.5	.88
	99.0	1.09

Evinrude 18 HP - Drained

RPM	DRAINAGE g/hr.	DRAINAGE - % FUEL
1500	74.3	4.31
2000	57.7	2.99
3000	46.7	1.53
4000	39.0	.66

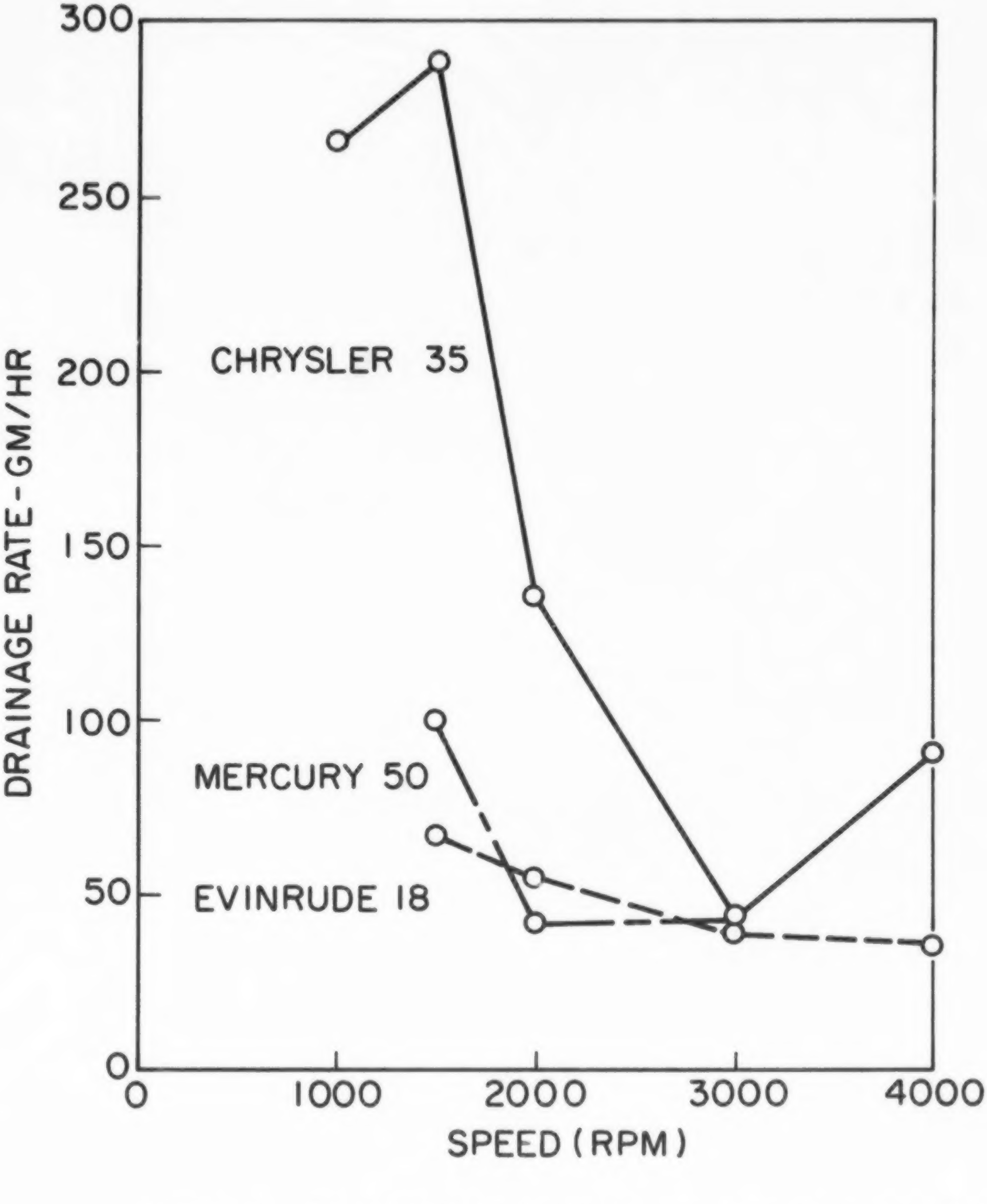


Figure 20 Drainage Rate in Grams per Hour as a Function of Engine Speed at the Boat-Load Test Conditions for 3 Engines with Crankcase Drainage.

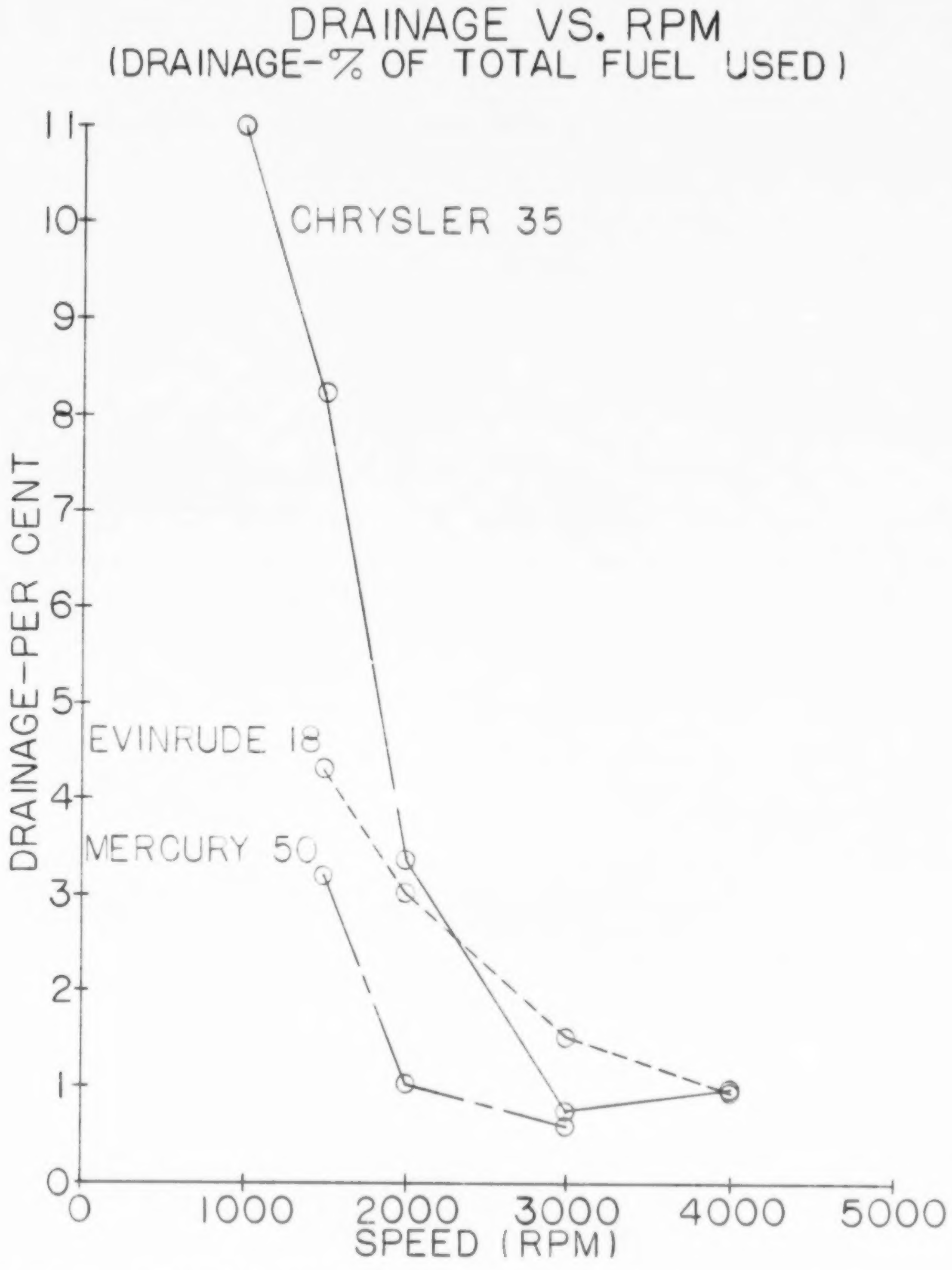


Figure 21 Crankcase Drainage Expressed as a Percentage of the Fuel Used as a Function of Engine Speed at the Boat-Load Test Conditions for 3 Engines with Crankcase Drainage

method consisted of constructing a viscosity - composition curve and using it to measure the viscosity of the drainage samples. Figures 22 through 25 give drainage composition data, showing that the oil composition of the crankcase was about 20-30% for all three engines. Since the ratio of oil to gasoline in the fuel was 1:50, crankcase drainage represents a 10-15 fold increase in oil content over the mixture fed to the engine.

Little or no difference was noted when comparing like engines of drained or drainless configuration with respect to both gaseous emissions (Figures 33 through 44, Appendix A) and condensable hydrocarbons (Table 10).

Influence of Maintenance on Two-cycle Marine Emissions

Two engines, 18 hp Evinrude and 35 hp Chrysler were investigated for the influence of maintenance on emission performance. Actually, these engines were a similar model and horsepower to two engines tested earlier but were engines being used by ENCOTEC for the pond study. The intent was to run the engines as received, perform normal maintenance and then rerun the engines again and compare the emission performance.

Unfortunately the Chrysler engine could not be run in the as-received condition and certain minimal maintenance procedures were required, including the replacement of bad spark plugs with a set of used but not completely fouled plugs. The results of this investigation are presented in a similar manner to those previously discussed.

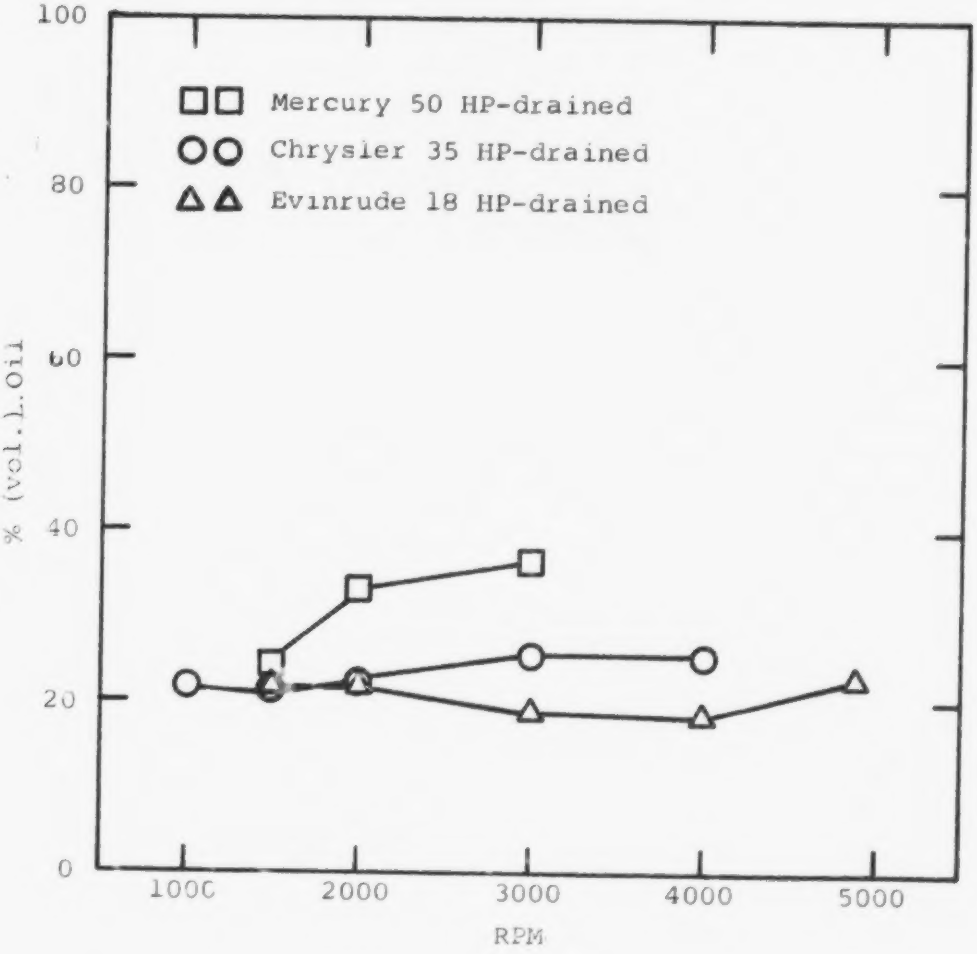


Figure 22 Percent Oil in Crankcase Drainage as Determined by Viscosity Measurement.

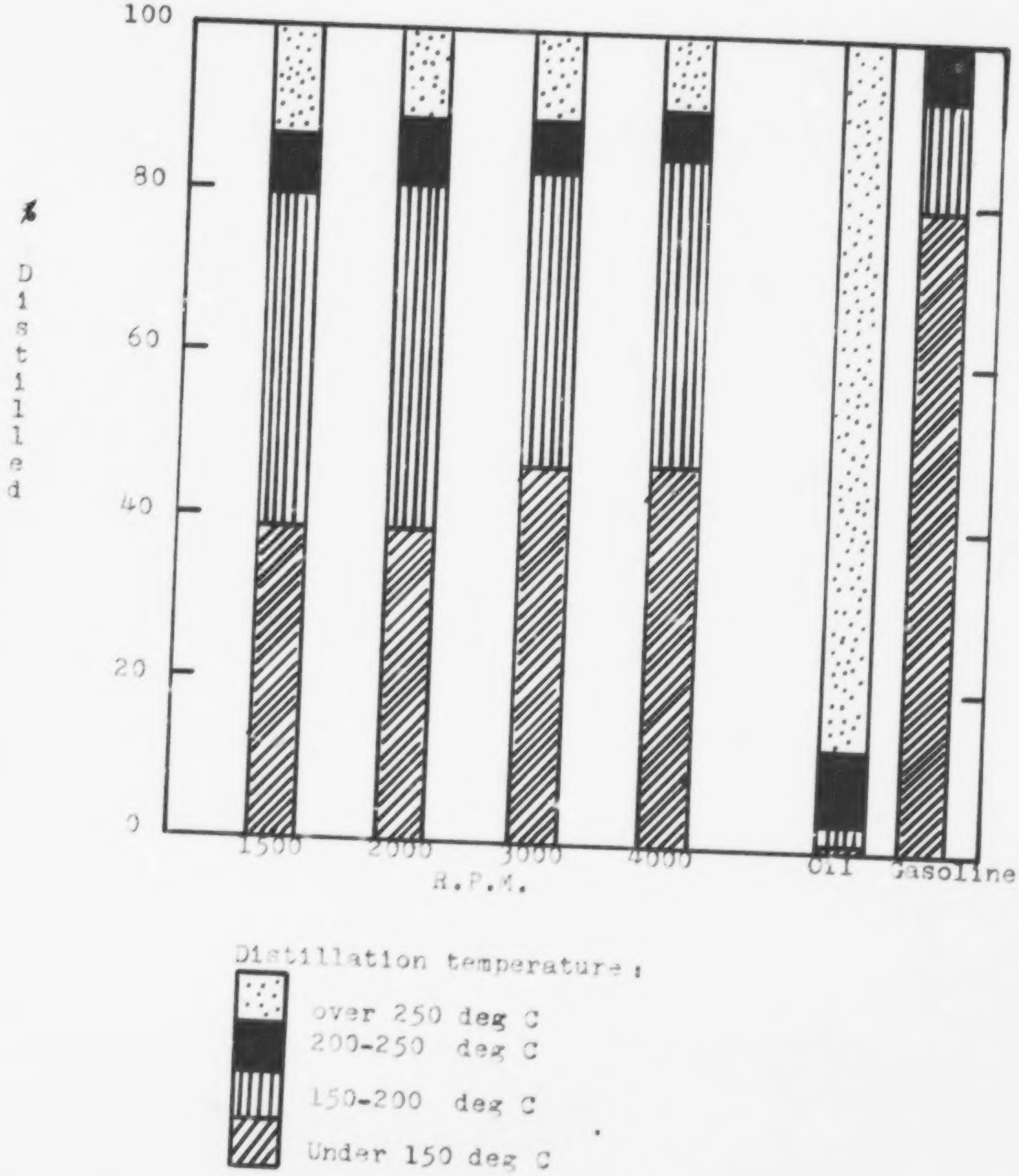


Figure 23 Boiling range analysis of crankcase drainage from Evinrude 18 HP

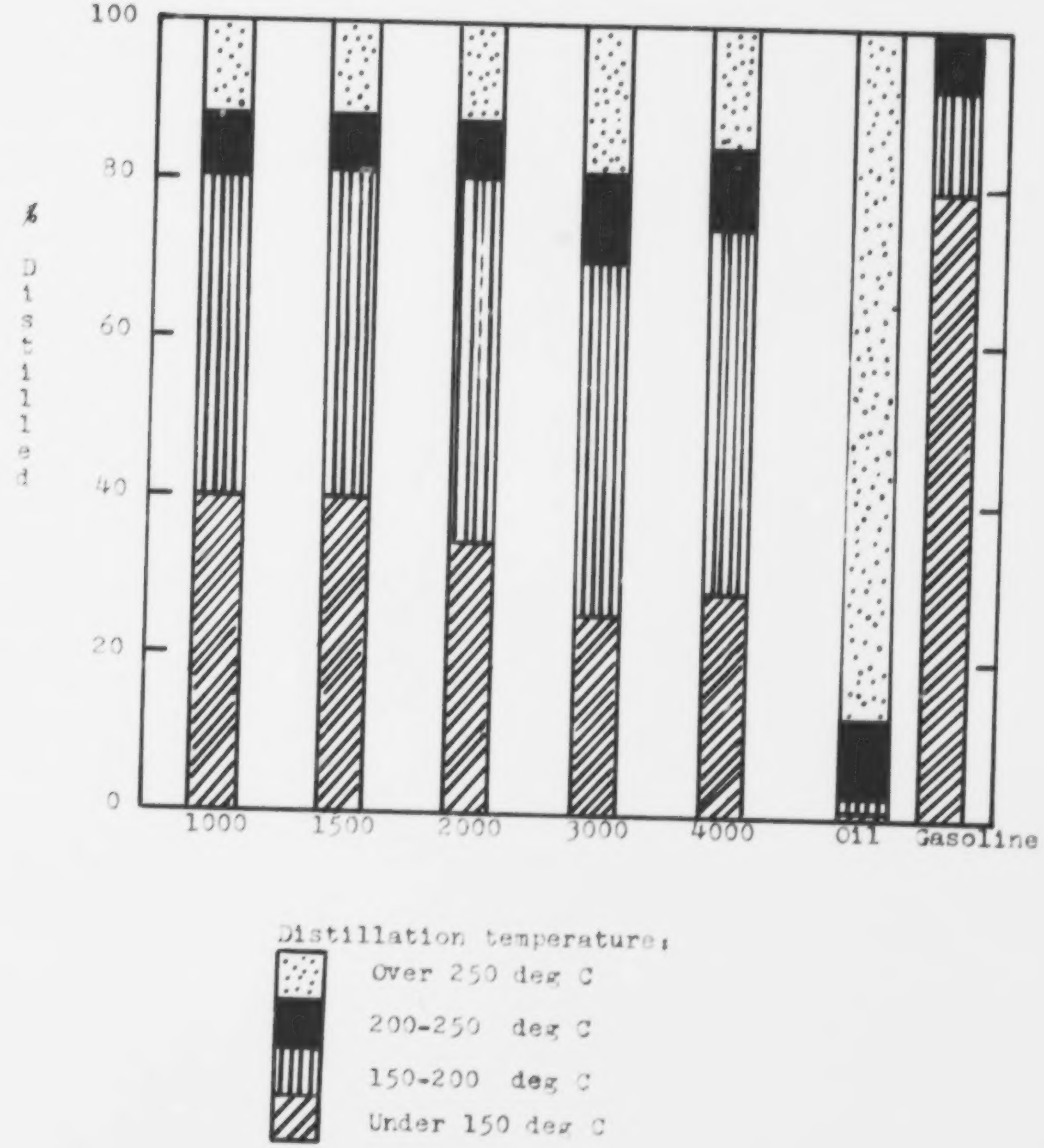


Figure 24 . Boiling Range Analysis of Crankcase Drainage from Chrysler 35 HP

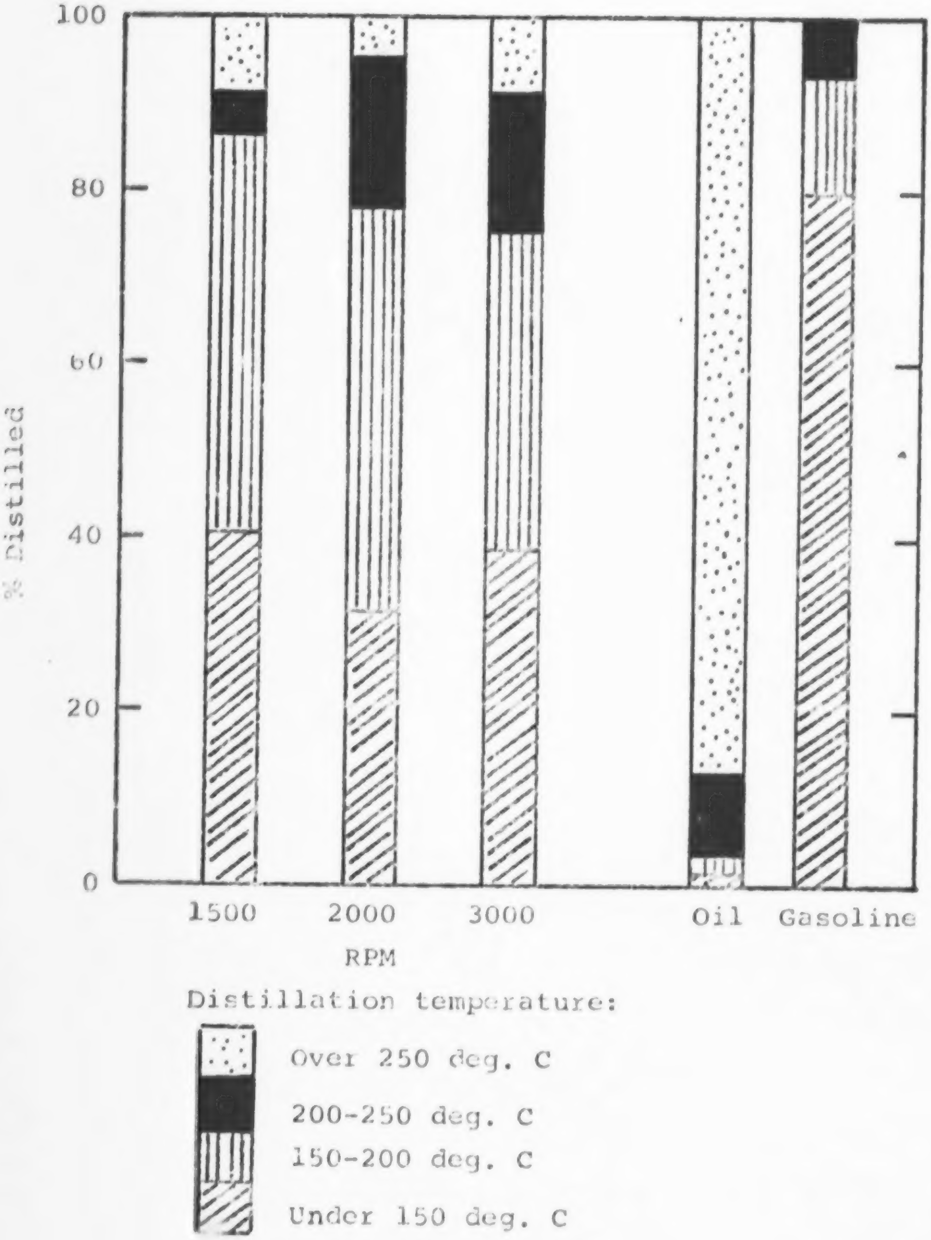


Figure 25 Boiling Range Analysis of Crankcase Drainage from Mercury 50 HP

The performance of these tuned and untuned engines are plotted in Figures 26 through 33. Clearly the maintenance procedures resulted in only very minor changes in emission performance. In some cases the emissions of undesirable pollutants did not decrease with maintenance.

One key to the change in the performance would have been indicated by a variation in fuel-air ratio from the untuned to tuned state. The ratio of the air-fuel ratio untuned to tuned is plotted in Figures 34 and 35 for the 18 hp Evinrude and 35 hp Chrysler engines. The maximum variation in the fuel-air ratio was only 4%. This is not a significant variation and supports the findings that there is a small difference in emission performance. It must be recognized that the sample size selected for this evaluation is small. Therefore, the results only suggest the likelihood that small variations occur in emission performance with maintenance or, stated another way, as the engine is used, only a small change in emission level is expected. A major change such as observed with the Chrysler engine with the fouled plugs would prevent the engine from running or at least the operational characteristics of the engine would be very undesirable and the operator would wuickly seek assistance.

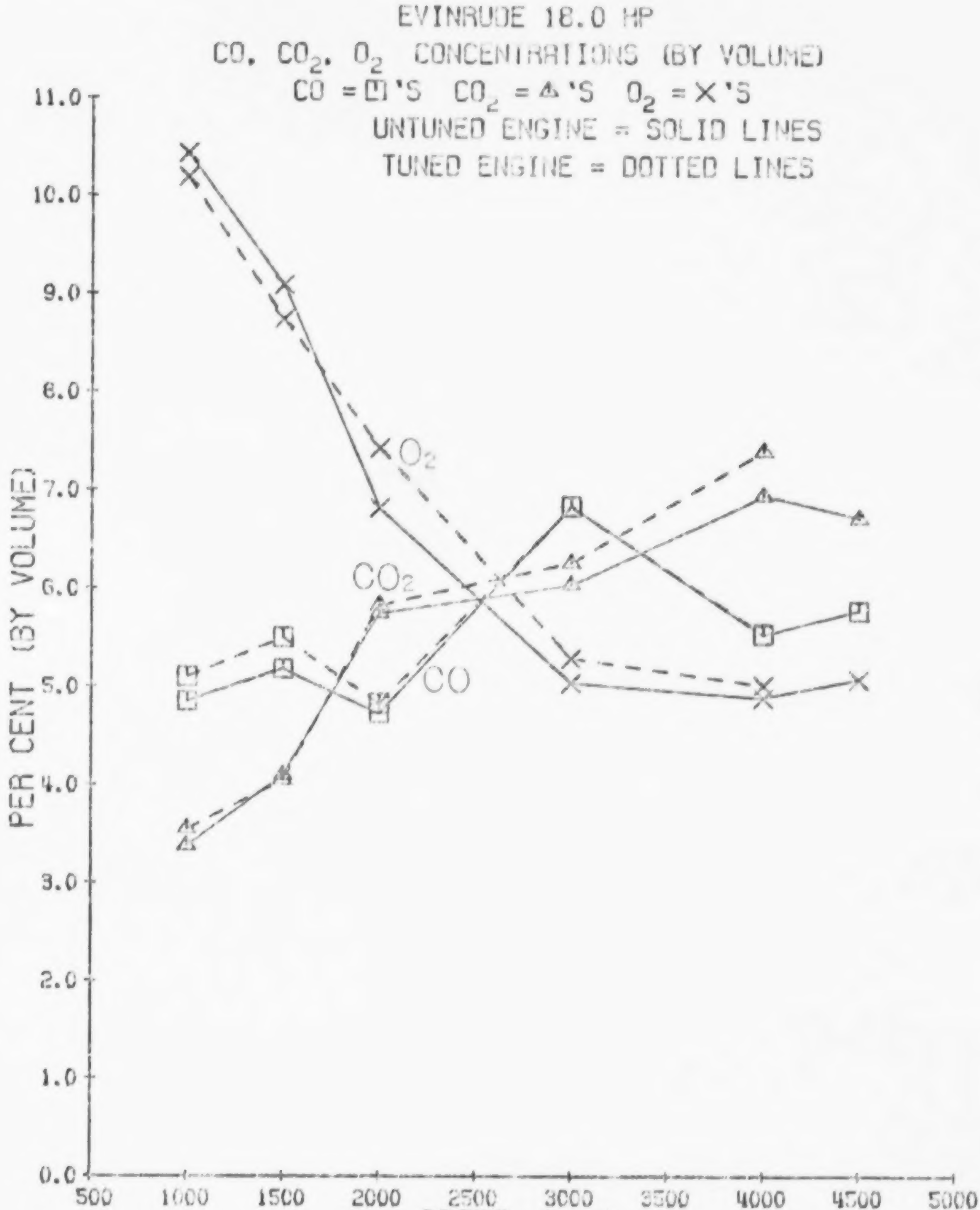


Figure 26 Effect of Maintenance on the CO, CO_2, and O_2 Concentration Emissions at the Boat-Load Test Conditions, 18 hp Evinrude

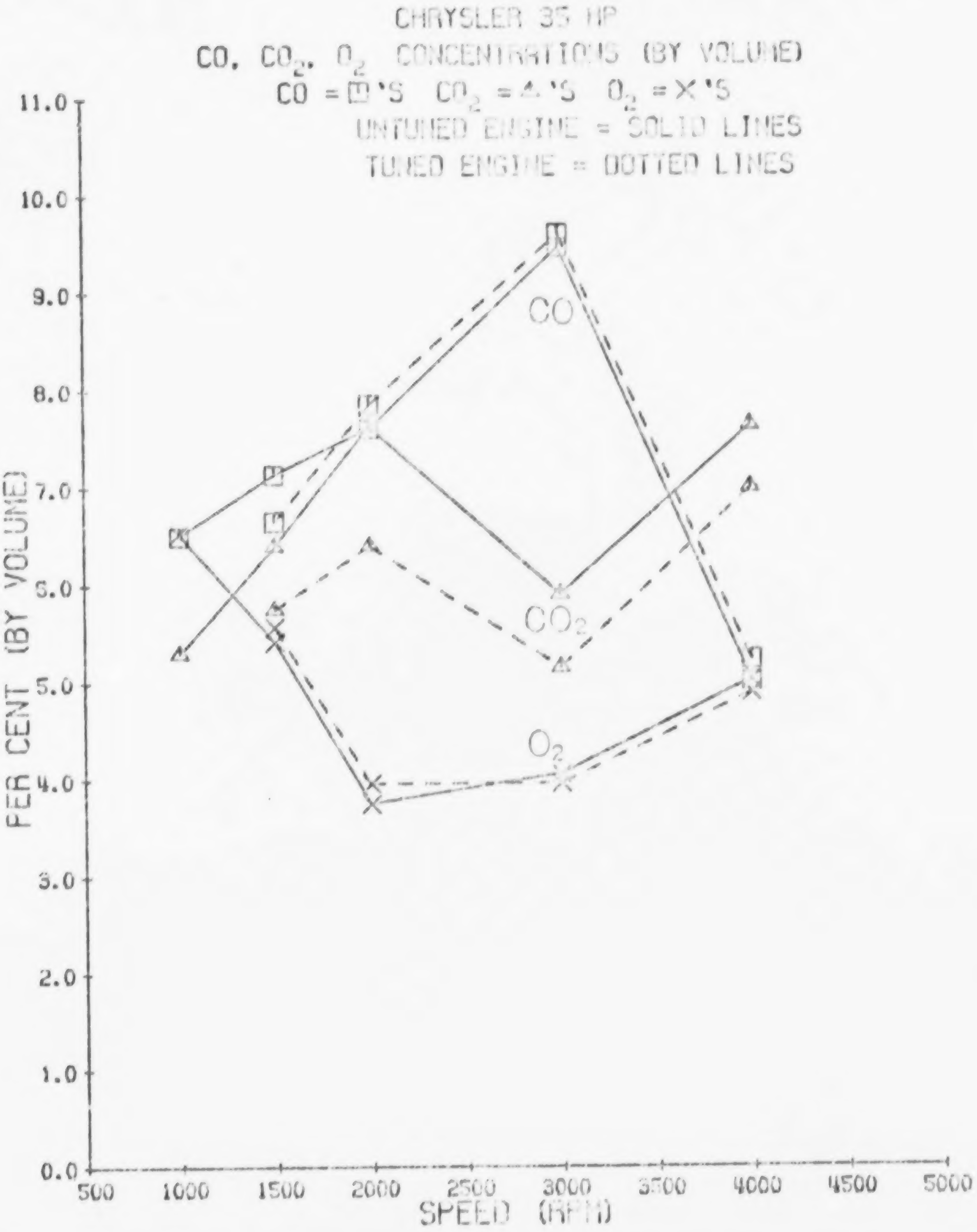


Figure 27 Effect of Maintenance on the CO, CO_2, and O_2 Concentration Emissions at the Boat-Load Test Conditions, 35 hp Chrysler

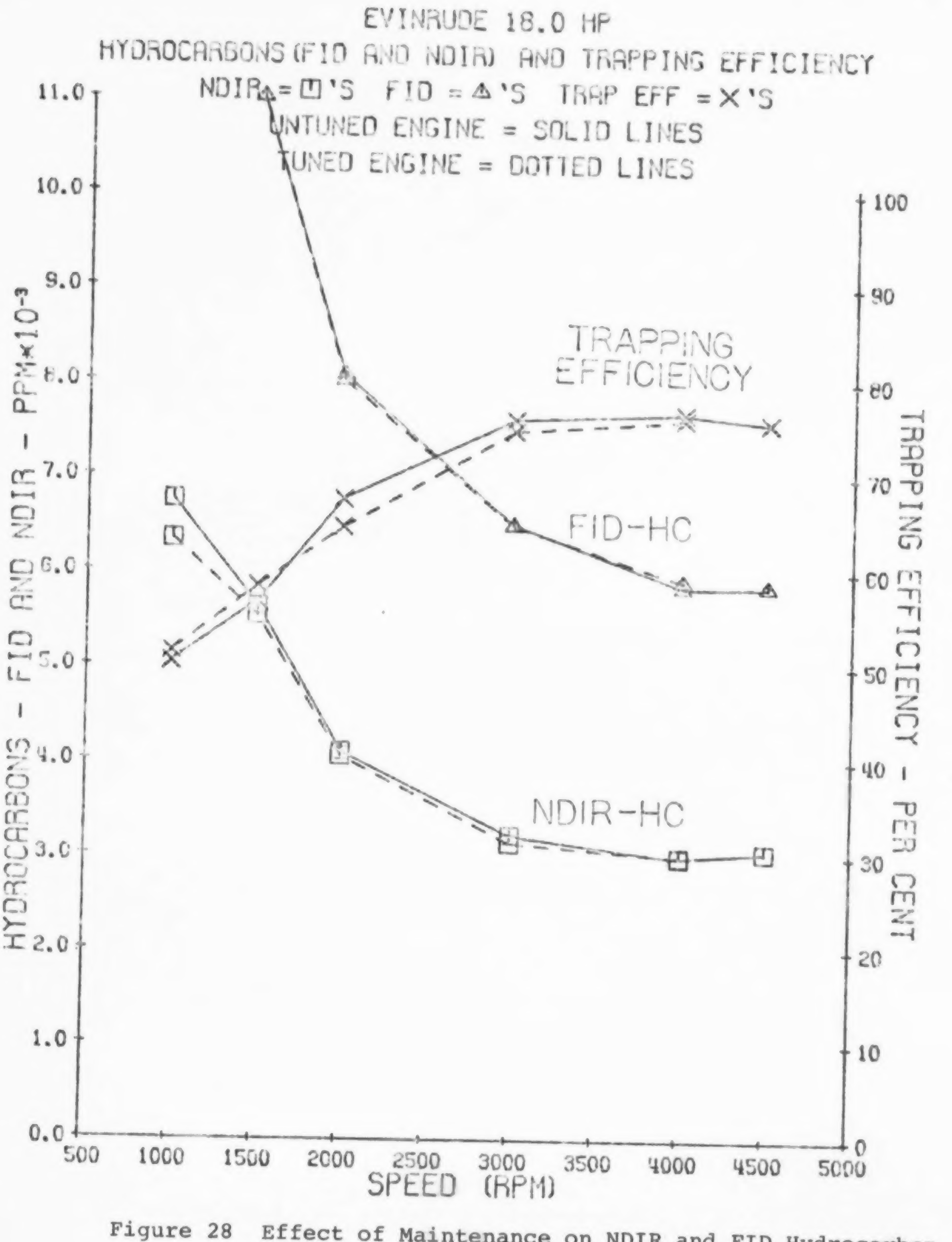


Figure 28 Effect of Maintenance on NDIR and FID Hydrocarbon Emissions and Trapping Efficiency at the Boat-Load Test Conditions, 18 hp Evinrude

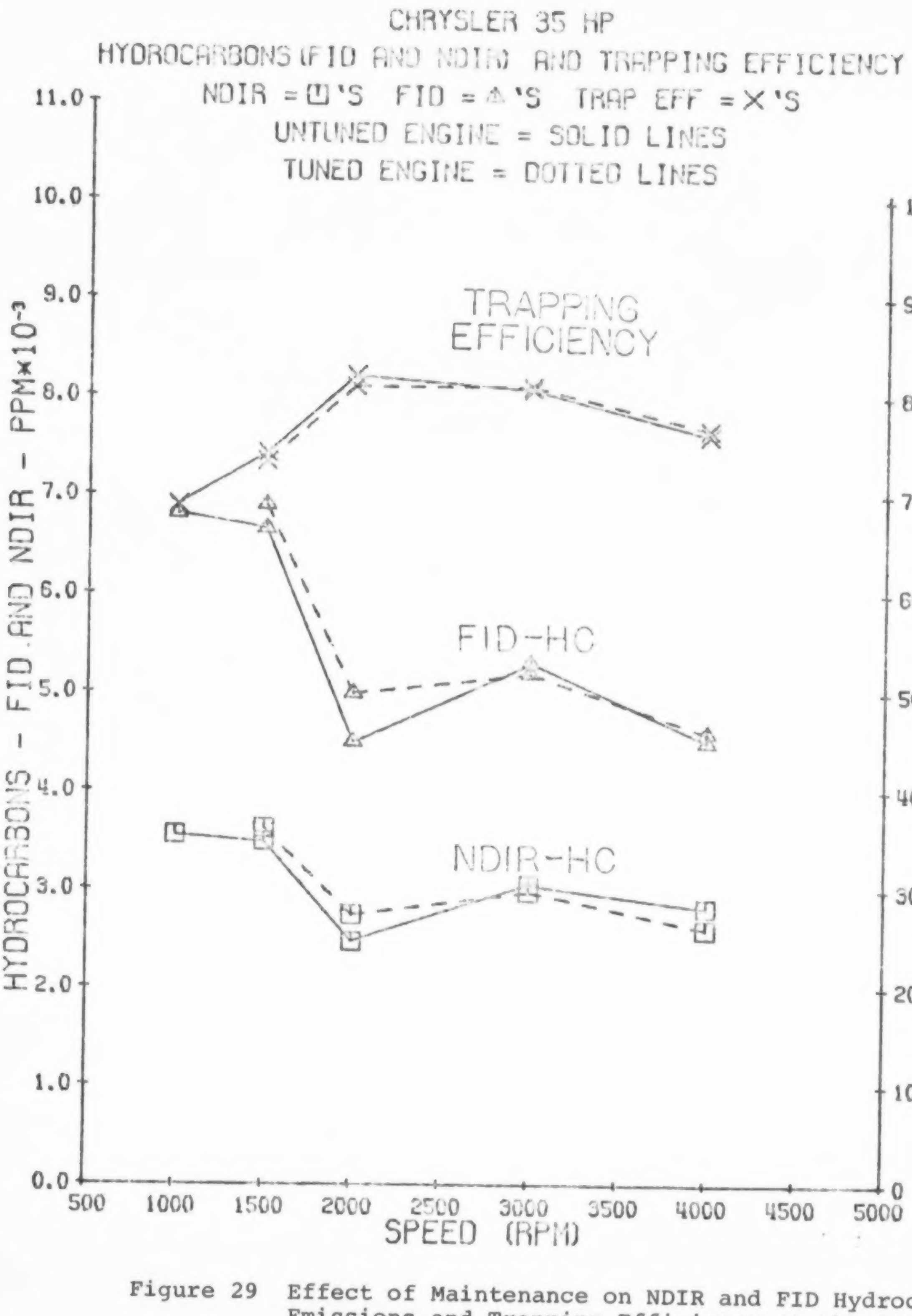


Figure 29 Effect of Maintenance on NDIR and FID Hydrocarbon Emissions and Trapping Efficiency at the Boat-Load Test Conditions, 35 hp Chrysler

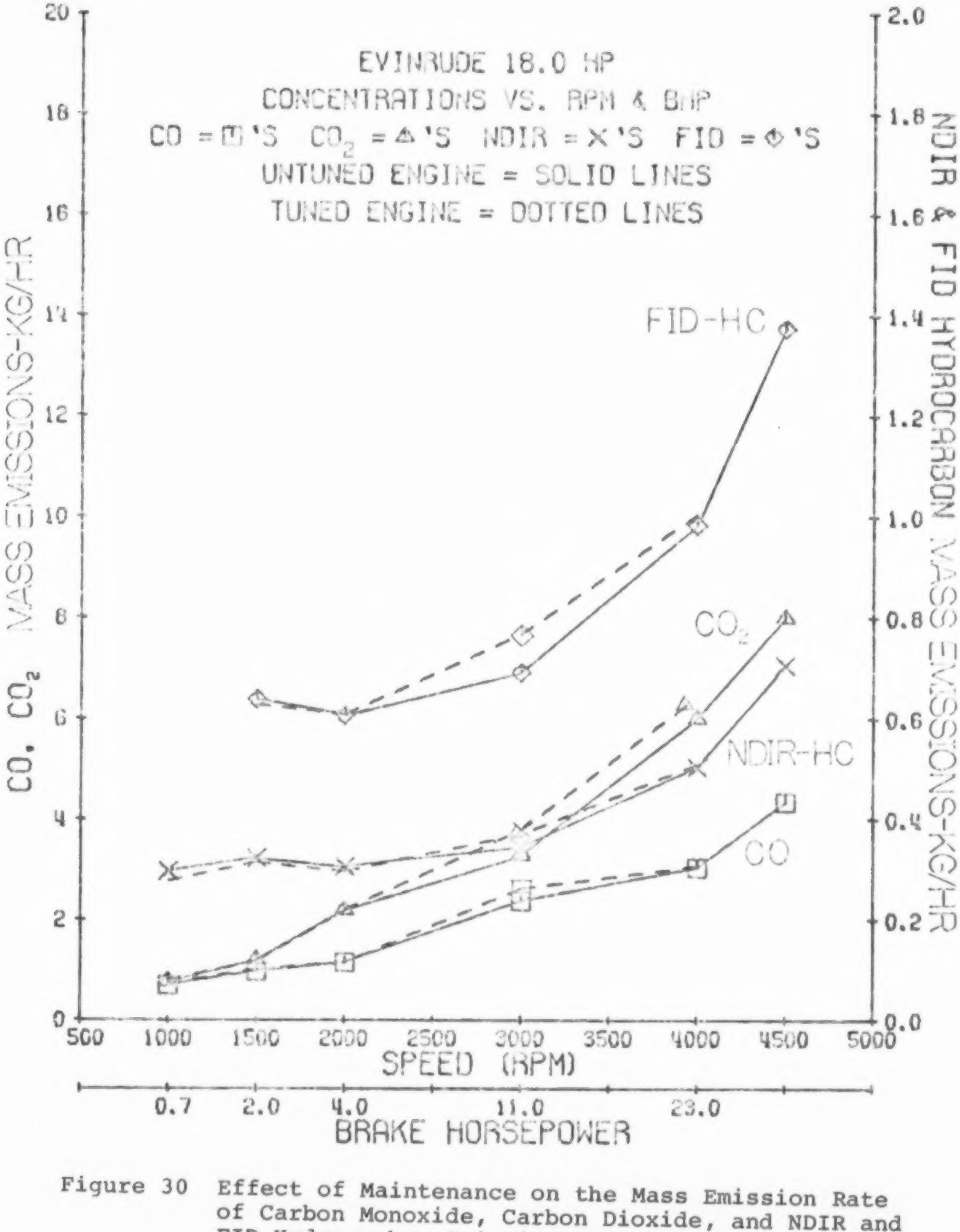


Figure 30 Effect of Maintenance on the Mass Emission Rate of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbon Emissions at the Boat-Load Test Conditions, 18 hp Evinrude

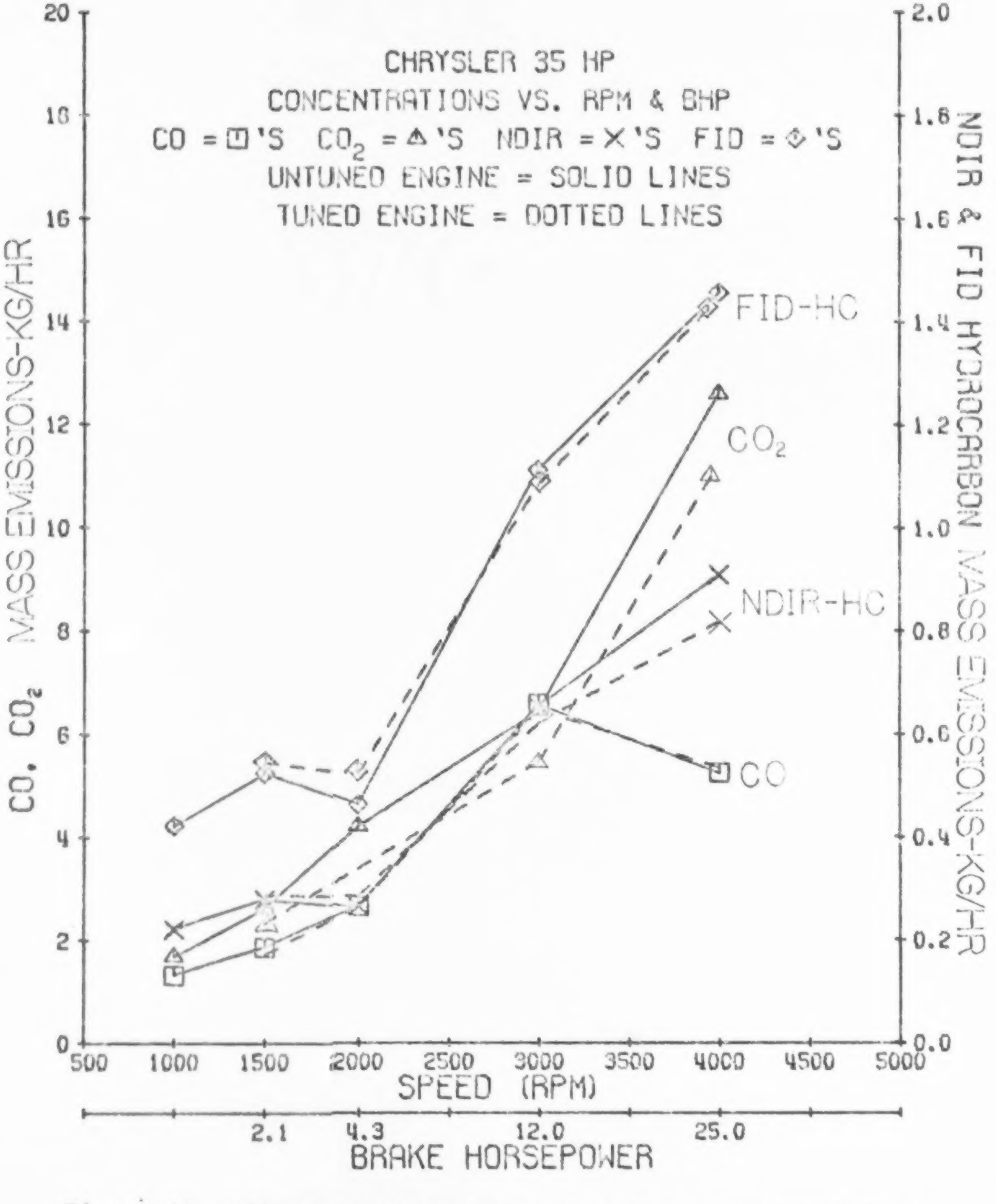


Figure 31 Effect of Maintenance on the Mass Emission Rate of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbon Emissions at the Boat-Load Test Conditions, 35 hp Chrysler

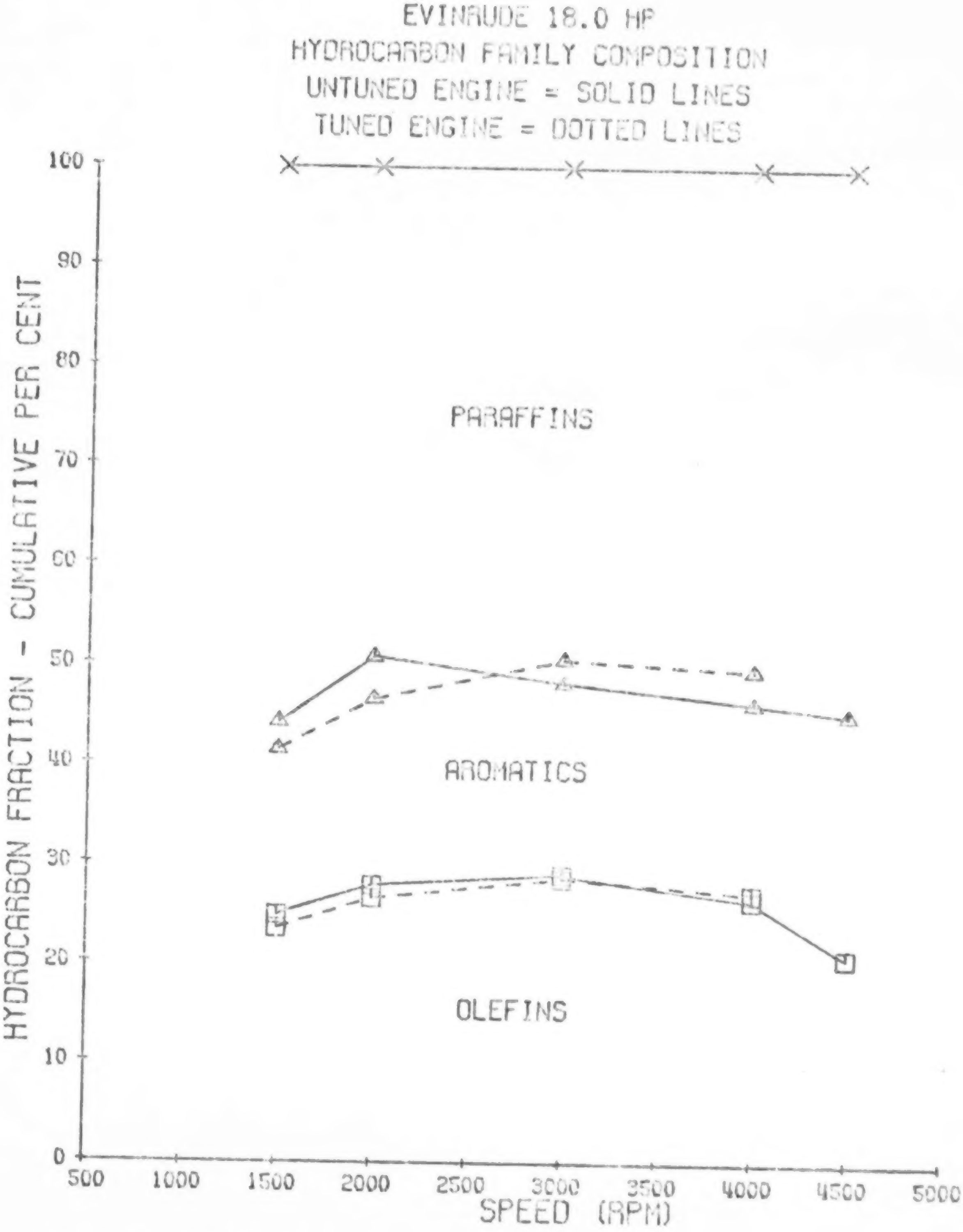


Figure 32 Effect of Engine Maintenance on the Family Hydrocarbon Composition at the Boat-Load Test Conditions, 18 hp Evinrude

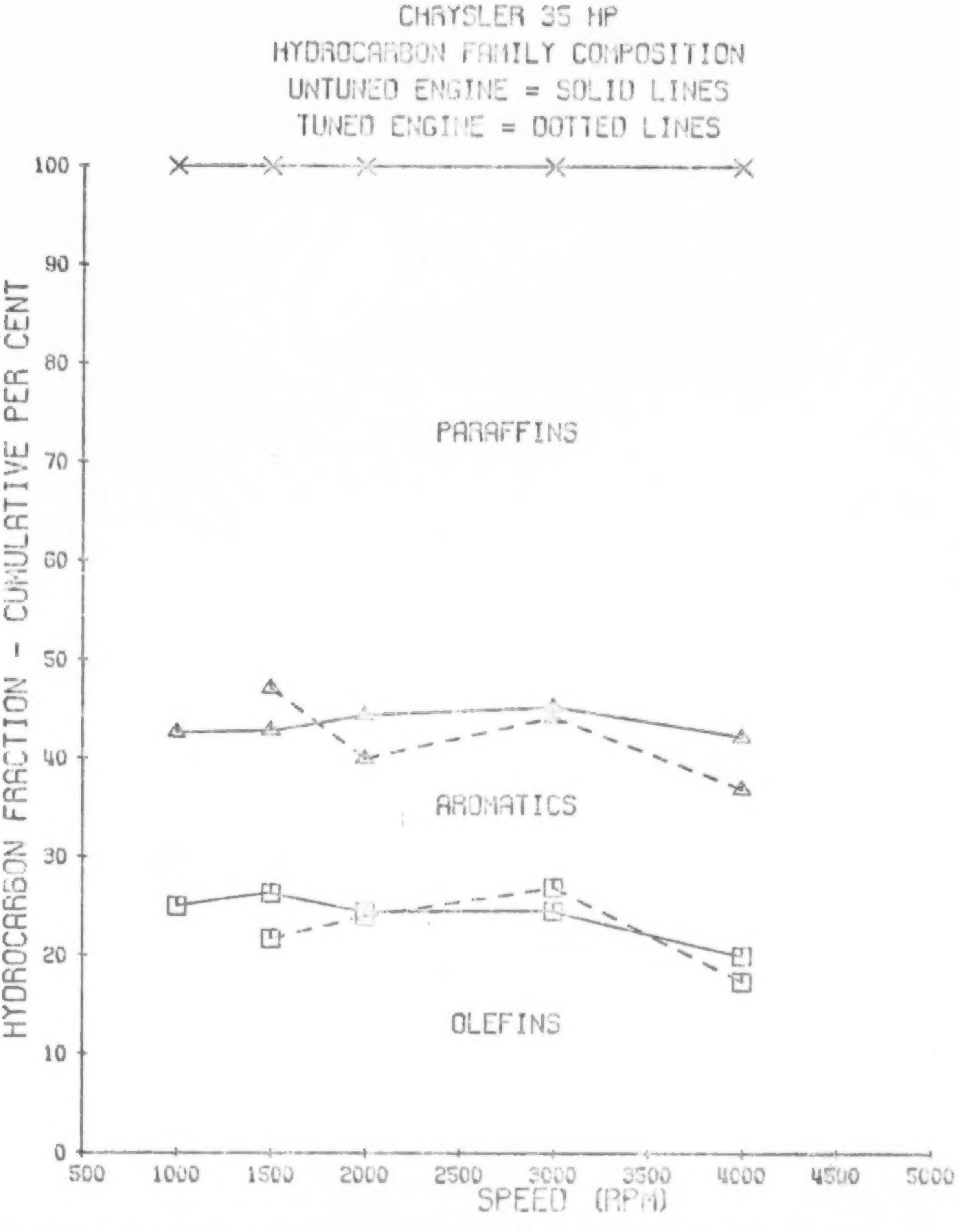


Figure 33 Effect of Engine Maintenance on the Family Hydrocarbon Composition at the Boat-Load Test Conditions, 35 hp Chrysler

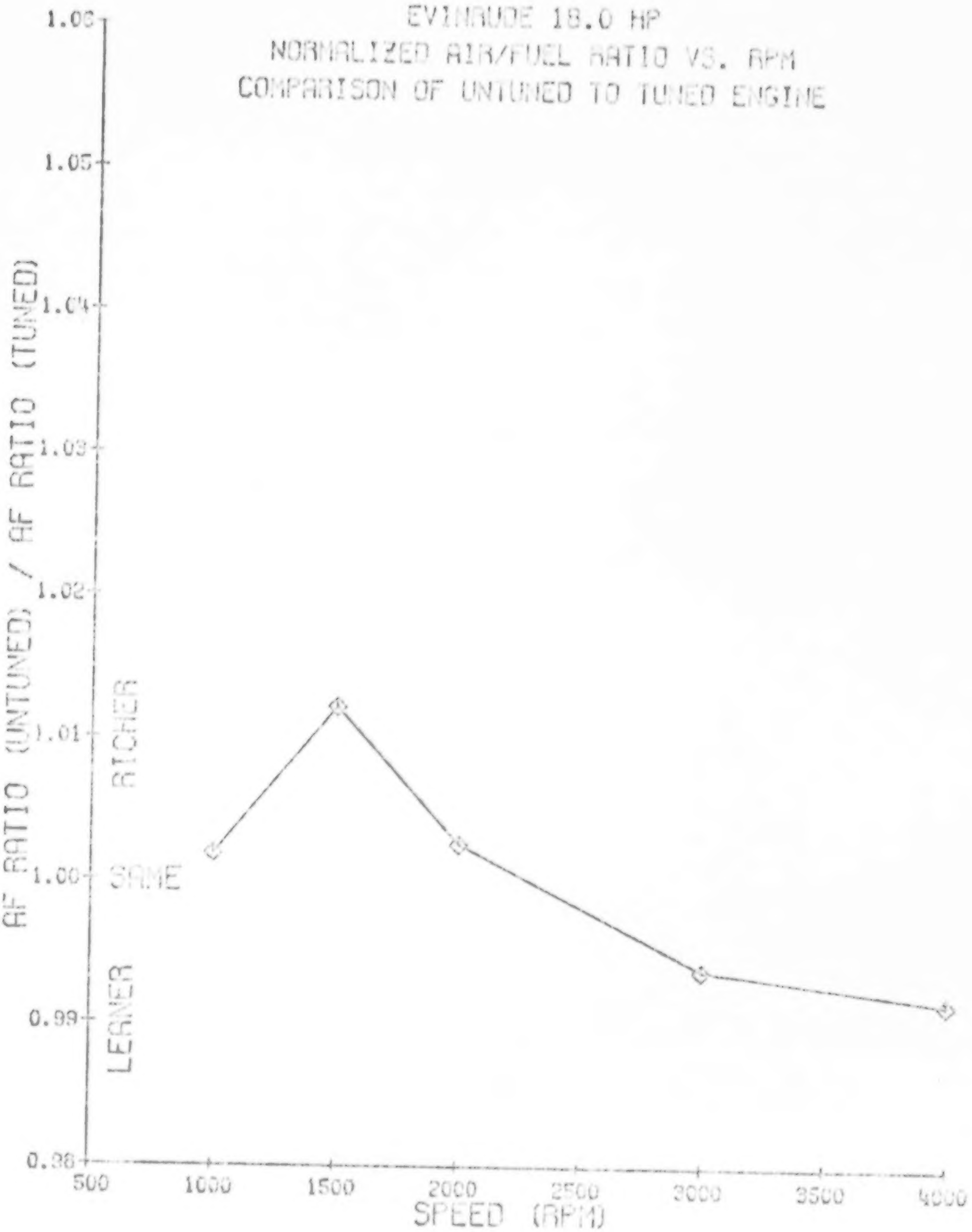


Figure 34 Effect of Maintenance on the Engine Fuel/Air Ratio at the Boat-Load Test Conditions, 18 hp Evinrude

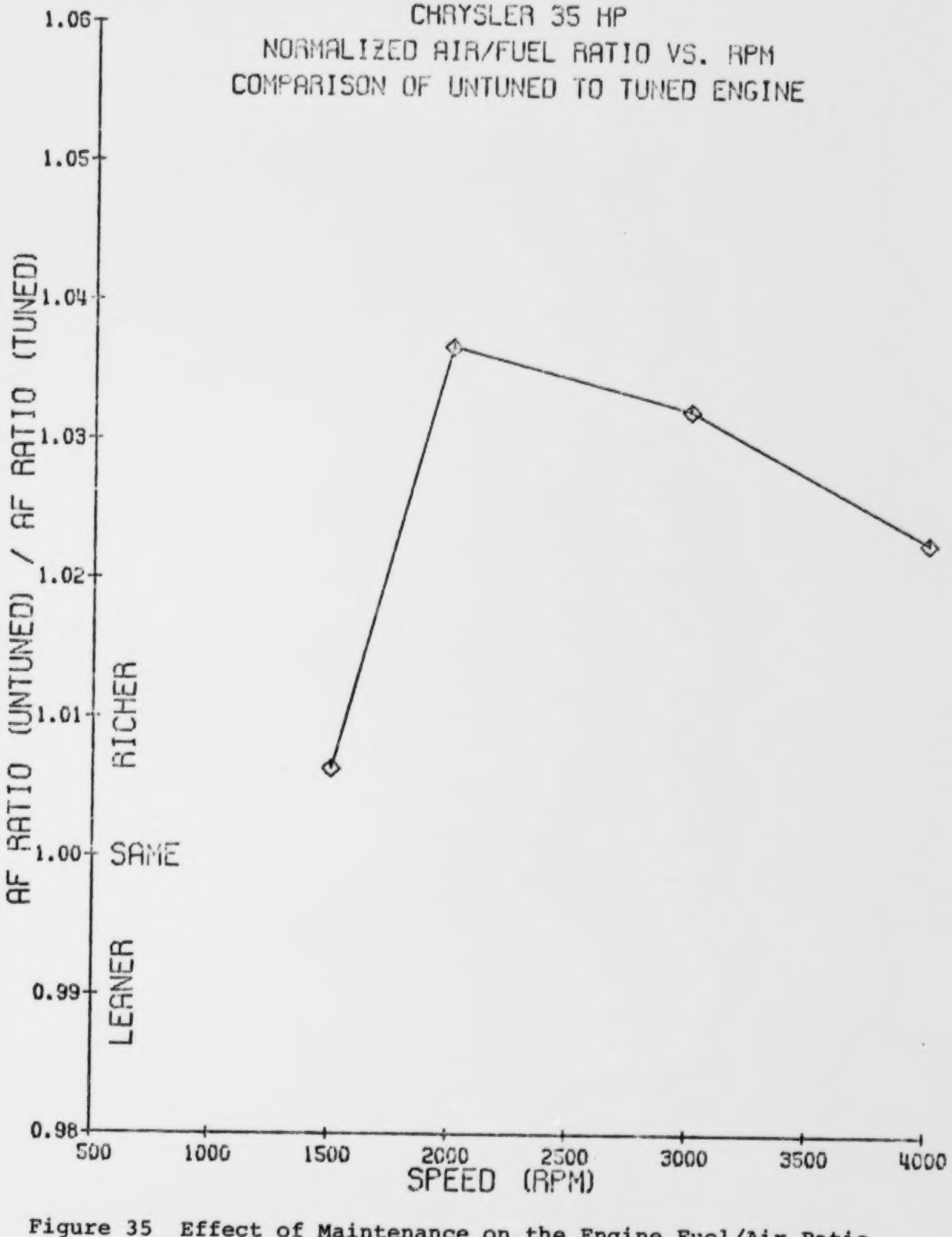


Figure 35 Effect of Maintenance on the Engine Fuel/Air Ratio at the Boat-Load Test Conditions, 35 hp Chrysler

The engines used in field testing also did not differ significantly from the corresponding new engines tested with respect to condensable emissions, as indicated by the data presented in Table 10. Indeed, the only trend toward a difference was exhibited by the 18 hp Evinrude engines, for which the field engine gave somewhat lower amounts of condensables than did the new one. This small difference may be accounted for by the fact that there are some differences to be expected even within a given engine model.

SECTION V

CONDENSABLE COMPONENTS

INTRODUCTION

The purpose of this part of the study was to collect and identify condensable fractions of outboard engine exhaust emissions under controlled laboratory conditions, in a manner such that the contribution of this fraction of the exhaust could be accurately assessed. As noted previously, condensable fractions are those most likely to be transferred from submerged exhaust emissions to the water column.

To this end, engines were mounted on test stands, as described in a previous section of this report. The exhaust was passed through the collection and gas-phase analysis system shown schematically in Figure 5. Collection of condensate samples required three hours of continuous engine operation at each test condition. The system was arranged so that a constant 2 cu. ft./hr. was passed through the condensation section. It was possible to calculate condensables in the total exhaust by measuring the hydrocarbon flux with and without the collection apparatus in operation. A detailed view of the condensate collection system is presented in Figure 36. It consisted of a cold-water condenser and a dry-ice acetone condenser in series with a collection vessel for each condenser. Since both the flow through the collection system and the total flow of exhaust were measured, the condensate collected represented a known fraction of the total exhaust.

EXPERIMENTAL METHODS

At the end of each run both condenser systems were washed down with a fixed volume of $CHCl_3$, and the condensates and washings from the two receivers combined. The resulting two-phase mixture was placed in a separatory funnel and the organic phase retained and analyzed. Due to the large condensing surface area and the low temperatures used in collecting the condensate. it is virtually certain that this system condenses at least as much -- and probably significantly more -- of the exhaust than would a column of water in a lake or other water body under normal engine usage. Consequently, the amounts reported herein should represent maximum potential pollution loads rather than average values.

The composition of the condensable organic portion of the exhaust has been shown to consist of three fractions:

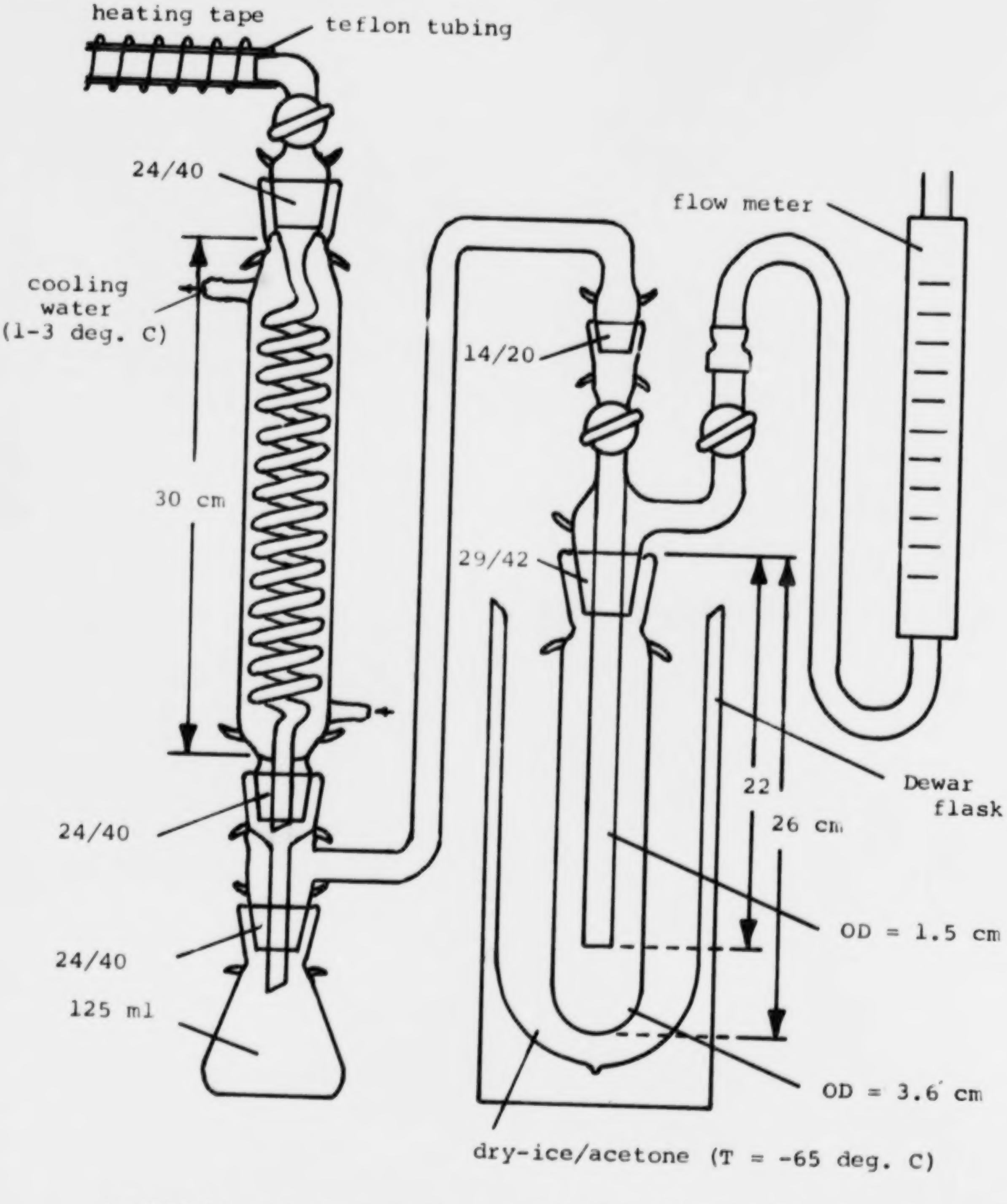

heating tape
teflon tubing
24/40
flow meter
cooling
water
(1-3 deg. C)
14/20
30 cm
29/42
Dewar
flask
22
26 cm
24/40
OD = 1.5 cm
24/40
125 ml
OD = 3.6 cm
dry-ice/acetone (T = -65 deg. C)

FIGURE 36 . Apparatus Used for Condensation of Outboard Engine Exhaust Gases.

unburned gasoline, partially oxidized hydrocarbons (i.e., phenols and carbonyl compounds) and unburned oil (5). Further, the unburned fuel is composed of three fractions: aromatics, olefins and paraffins. Since it has been established that aromatic compounds constitute the most important of these in terms of acute toxicity to aquatic life (18). primary attention was directed to the qualitative and quantitative analysis of this fraction.

The condensates were analyzed for aromatic hydrocarbons, olefins, phenols, carbonyl compounds and in one case for total condensable organic material. The analytical methods which were used are described below.

Aromatic Hydrocarbons

Samples of the fuel, of the condensate and of pure compounds known to be present in the fuel were examined first by infrared spectrophotometry. In the region from 12-15 μ there are out-of-plane C-H deformation vibrations characteristic of the substitution pattern on the benzene nucleus (19). Comparison with known compounds allowed a tentative assignment of the bands in this region, as shown in Figure 37. However, since this method is dependent on substitution pattern it is not specific for compounds; i.e., ethyltoluene would be expected to have the same bands as the corresponding

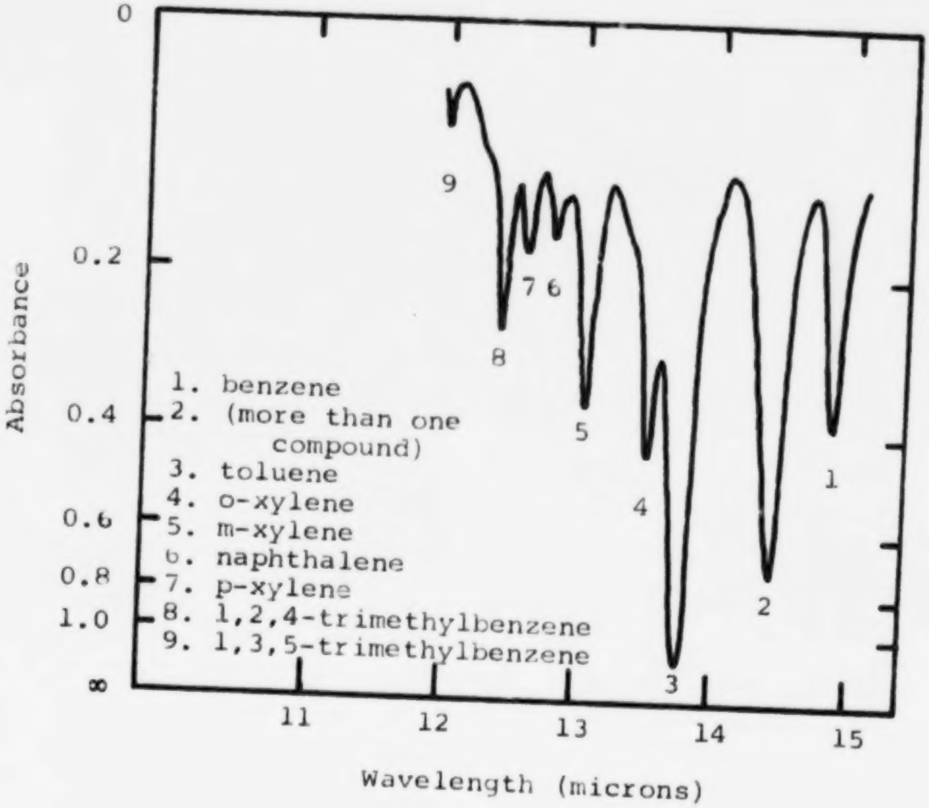


Figure 37 Infrared Spectrum of Indolene Clear Fuel in Cyclohexane Showing Absorbances due to Aromatics

xylene. A more rigorous identification method was needed and gas chromatography was selected. Gas chromatography was performed on a Varian 1700 instrument equipped with flame ionization detector using helium as carrier gas. Separations could be done using a 10 ft., 1/8 in. SS column packed with 3% PMPE on 80/100 Chromosorb W. Column temperature was isothermal at 100 °C and carrier gas flow rate was 30 ml/min. Retention times for pure aromatic species were compared with those present in the condensate sample. Results are presented in Figure 38. As a further verification of the assignment of the major peaks, a gas chromatograph coupled to a mass spectrometer, DuPont Model 21-490, was used. The mass spectra obtained for each of the major peaks were compared to existing files and confirmed the identification previously made by retention time measurements. Results are presented in Table 8 . Total condensable aromatic hydrocarbons were calculated by integrating the area under the identified peaks and applying the appropriate molar response factor. Results are presented in Table 10. A comparison of the ratio of toluene to other aromatics in the condensate and in the fuel showed that in most cases the ratio was lower in the condensate, suggesting that toluene was preferentially burned. See Figures 39-47.

Binuclear aromatic hydrocarbons were also detected in

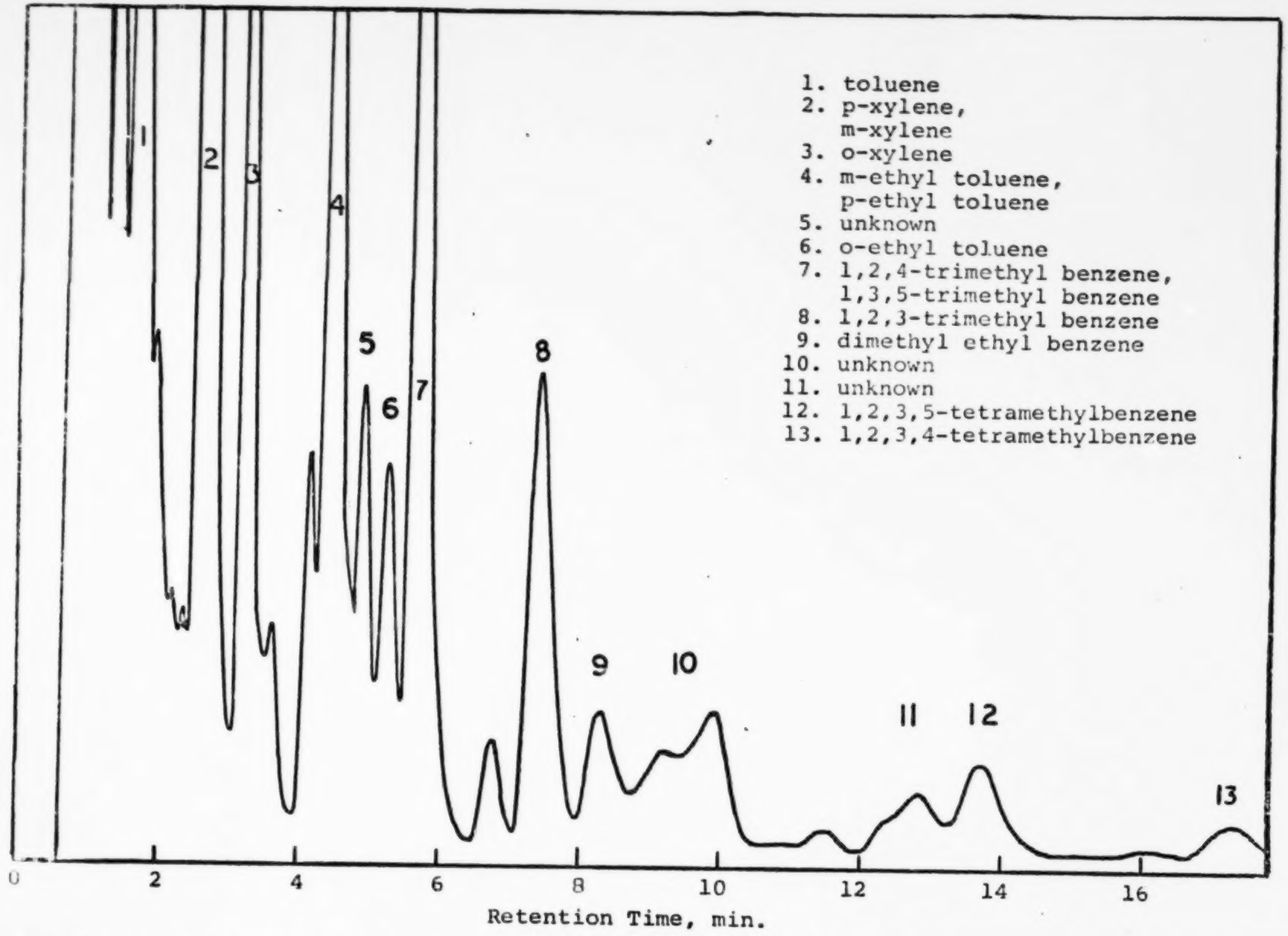


Figure 38 Typical Gas Chromatogram of Outboard Engine Exhaust Condensate. (Solvent: $CHCl_3$. Analytical conditions: PMPE column at 100 deg. C.; He flow rate, 30 ml/min.)

Condensate Peak Number	Mass Spectral Identification	Retention time (min.)	Pure Compound	Retention time (min.)
1	Toluene	1.60	Toluene	1.60
2	Xylene	2.66	*p*-Xylene	2.53
			m-Xylene	2.66
3	Xylene	3.20	*o*-Xylene	3.20
4	Ethyltoluene	4.33	*p*-Ethyltoluene	4.33
			m-Ethyltoluene	4.33
5	Unknown	5.00		
6	Ethyltoluene	5.20	*o*-Ethyltoluene	5.20
7	Trimethylbenzene	5.70	1,2,4-Trimethylbenzene	5.70
			1,3,5-Trimethylbenzene	5.70
8	Trimethylbenzene	7.40	1,2,3-Trimethylbenzene	7.40
9	Dimethyl-ethylbenzene	8.10	1,3-Dimethyl-5-ethylbenzene	8.10
10	Unknown	9.80		
11	Unknown	11.70		
12	Tetramethylbenzene	14.20	1,2,3,5-Tetramethylbenzene	14.20
13	Tetramethylbenzene	17.80	1,2,3,4-Tetramethylbenzene	17.80

Table 8 Mass Spectral Identification of Aromatic Hydrocarbons Present in Condensate, With Verification by Retention Time. (Analytical Conditions: PMPE column at 100 deg. C; He flow rate 30 ml/min.)

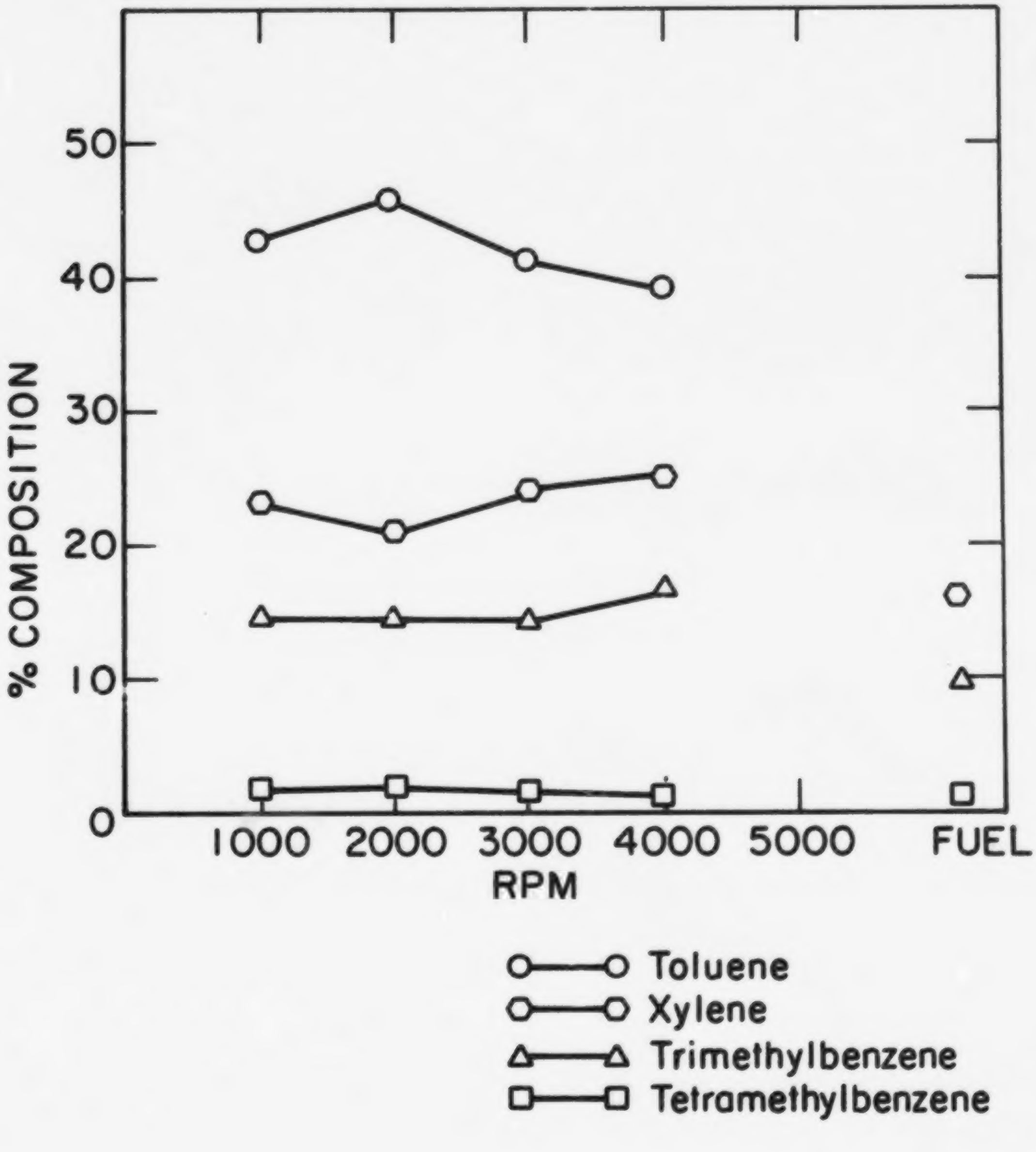


Figure 39 Aromatic Composition from Evinrude 6 HP.

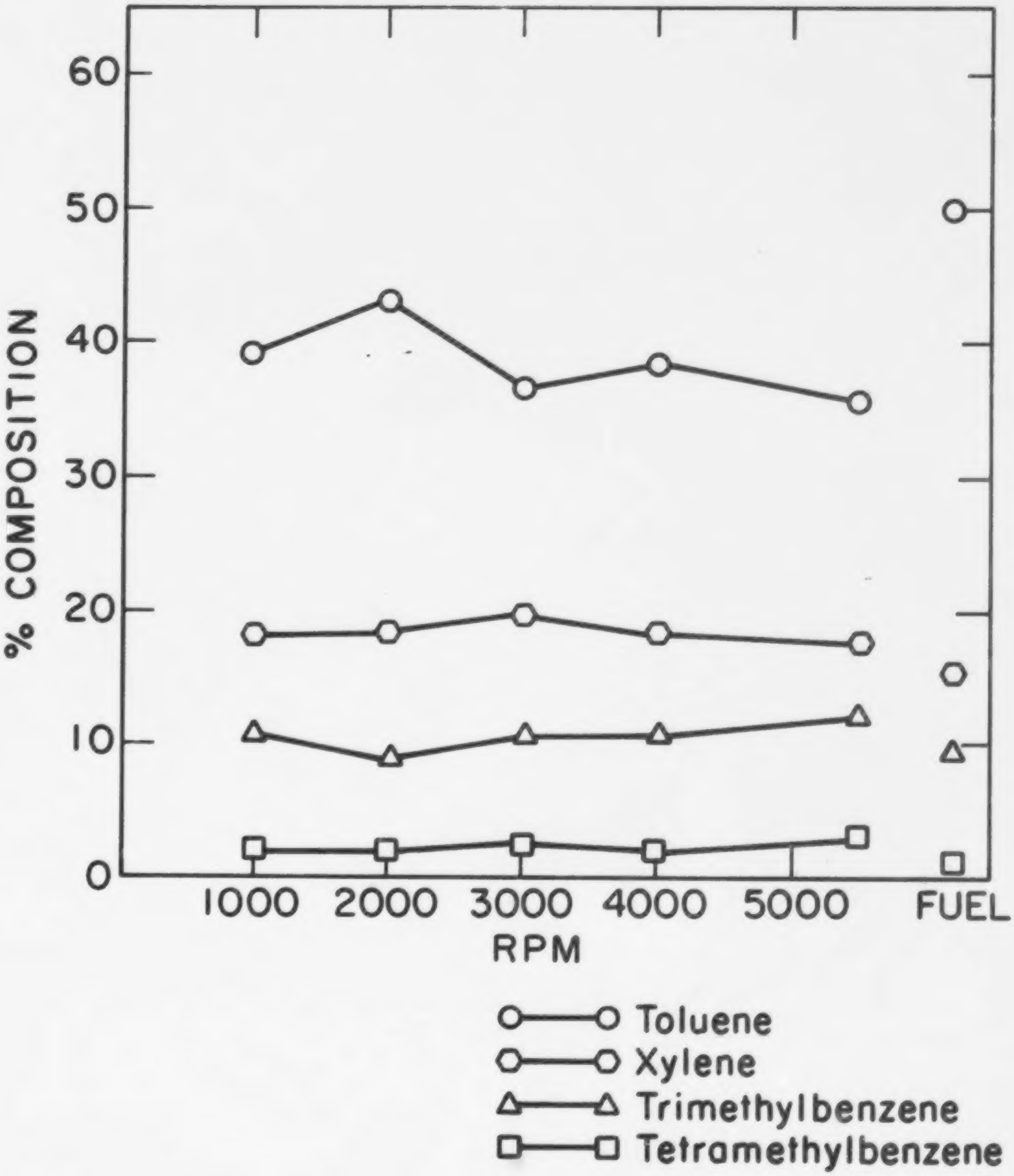


Figure 40 Aromatic Composition from Eska 7 HP.

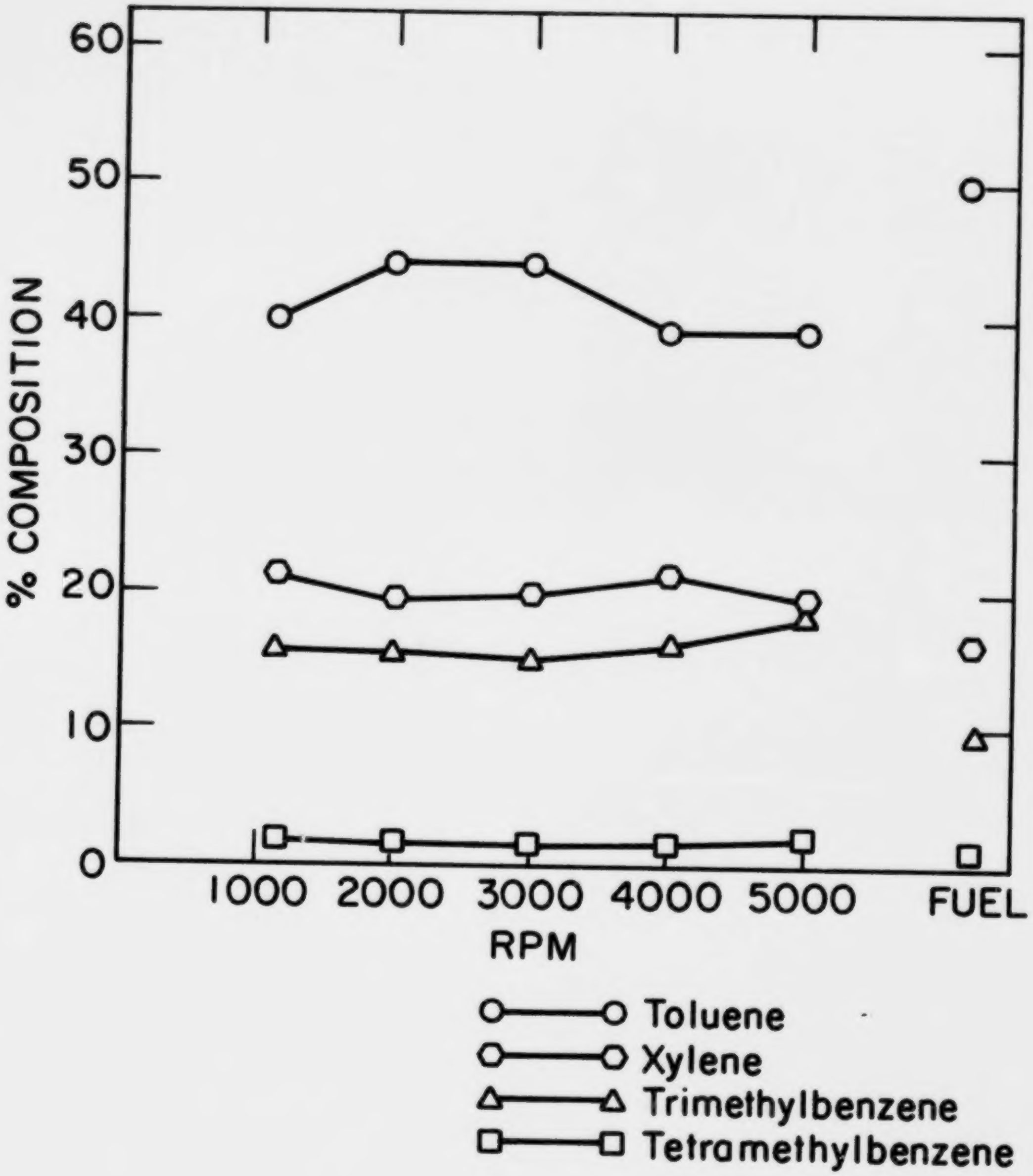


Figure 41 Aromatic Composition from Chrysler 12.9 HP.

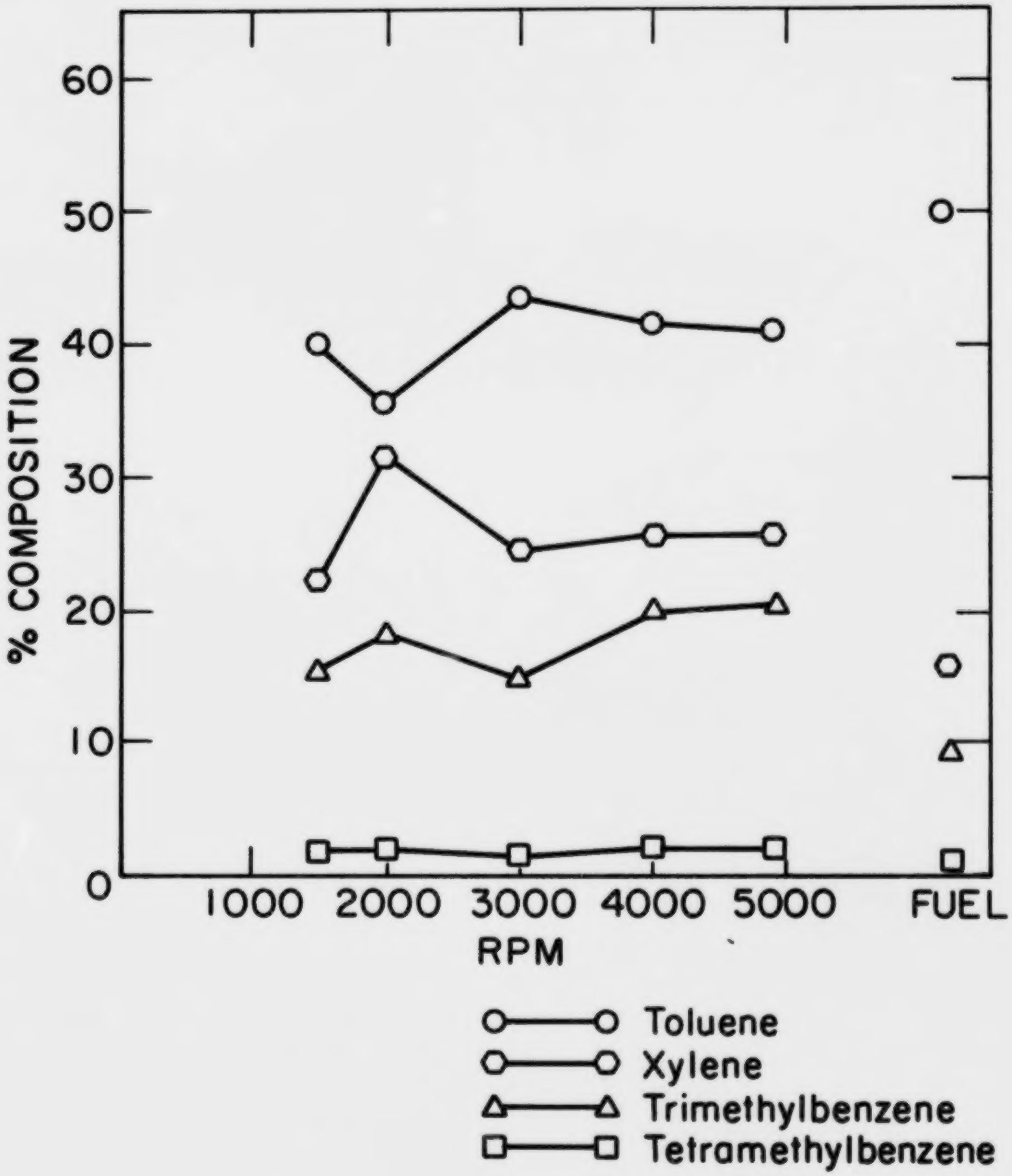


Figure 42 Aromatic Composition from Evinrude 18 HP.

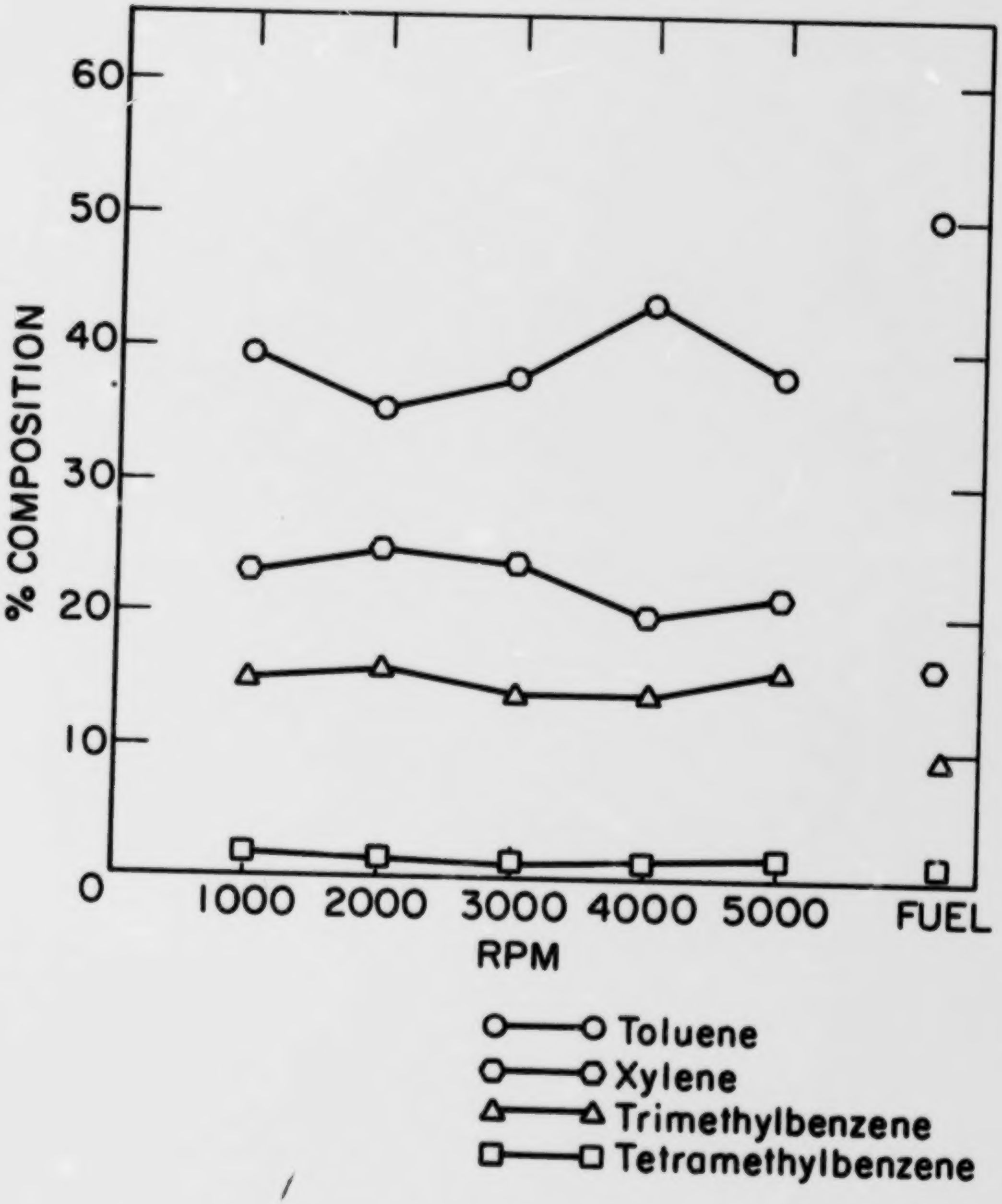


Figure 43 Aromatic Composition from Evinrude 18 HP (Drained).

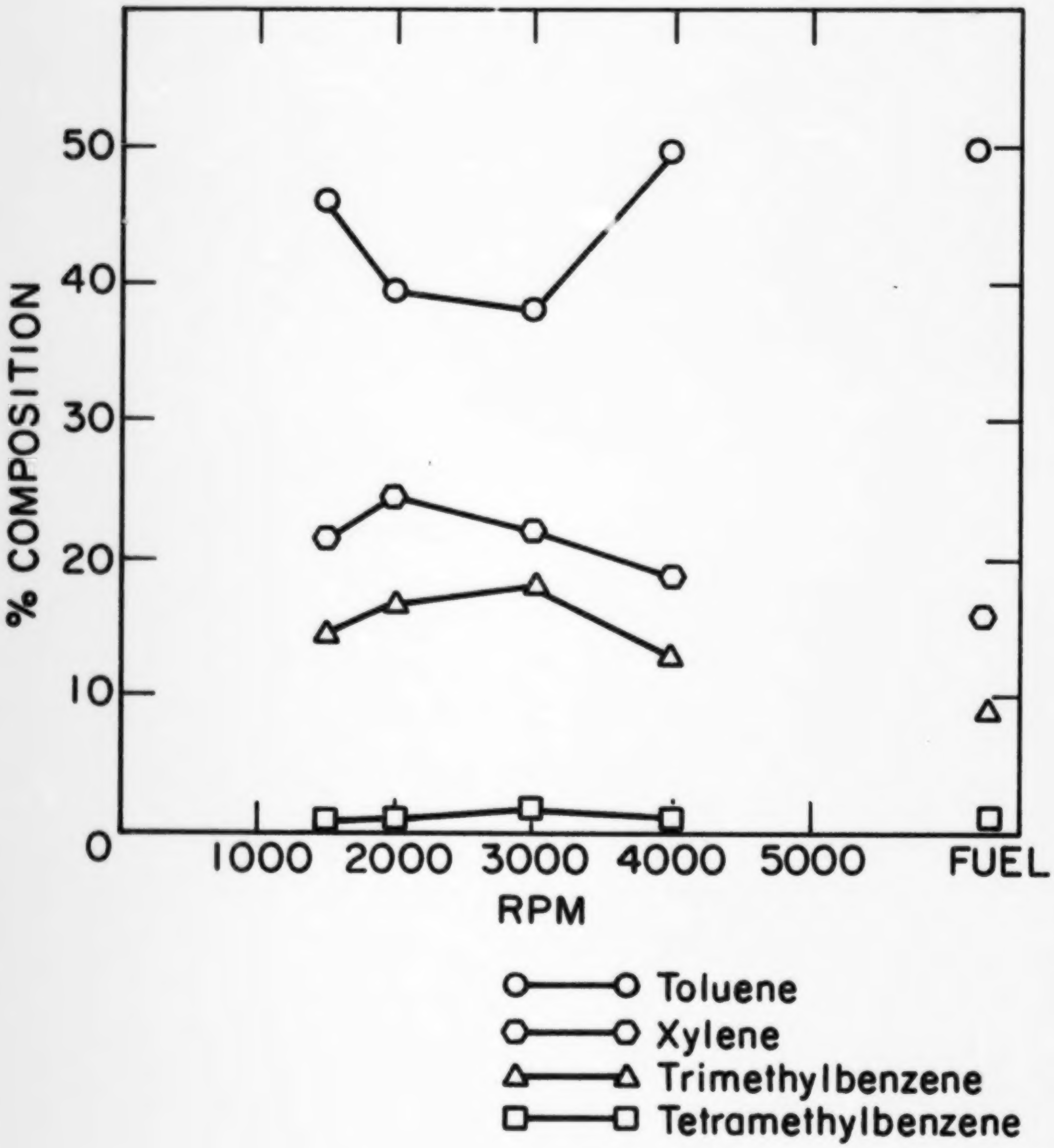


Figure 44 Aromatic Composition from Chrysler 35 HP.

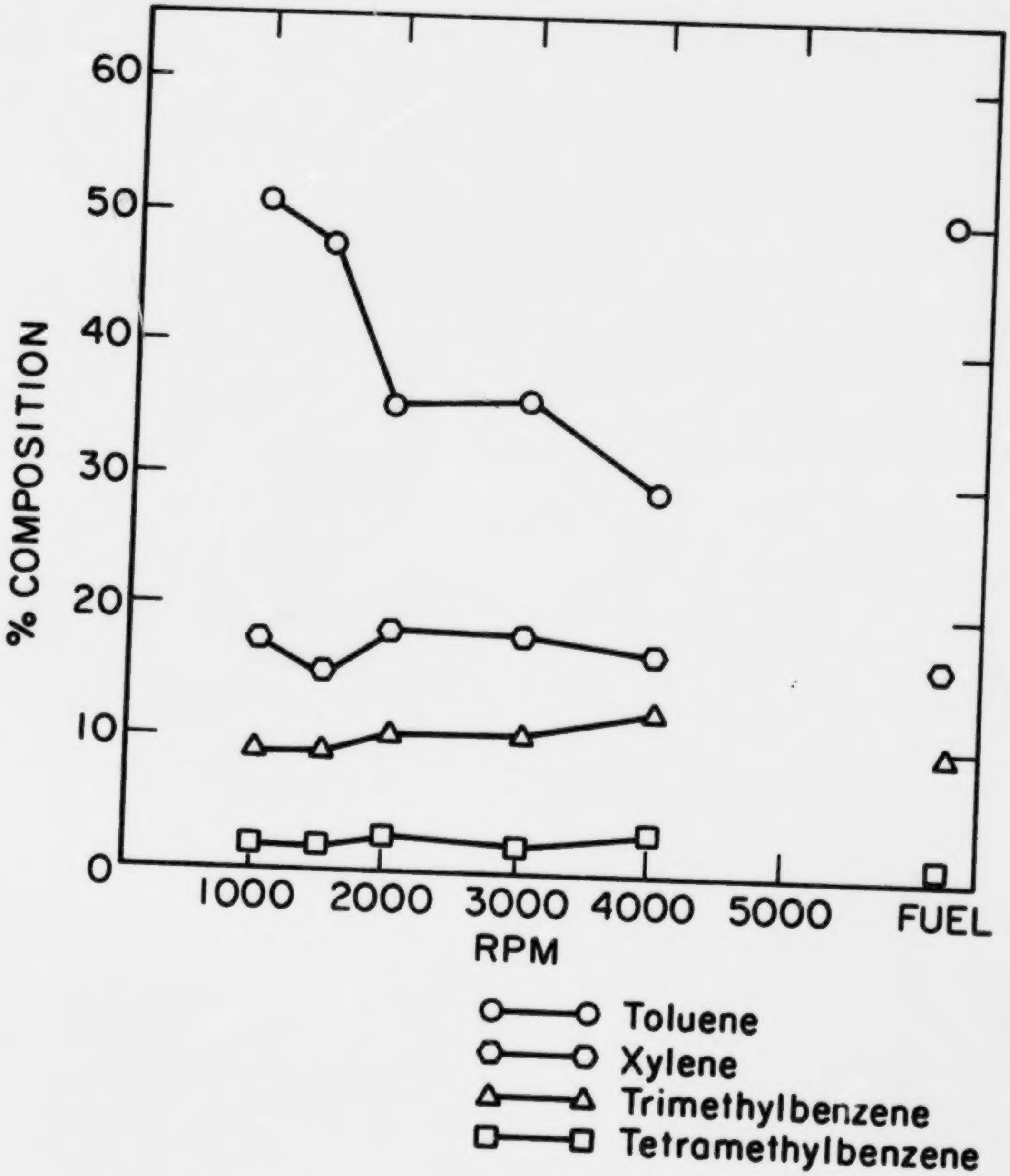


Figure 43 Aromatic Composition from Chrysler 35 HP--drained.

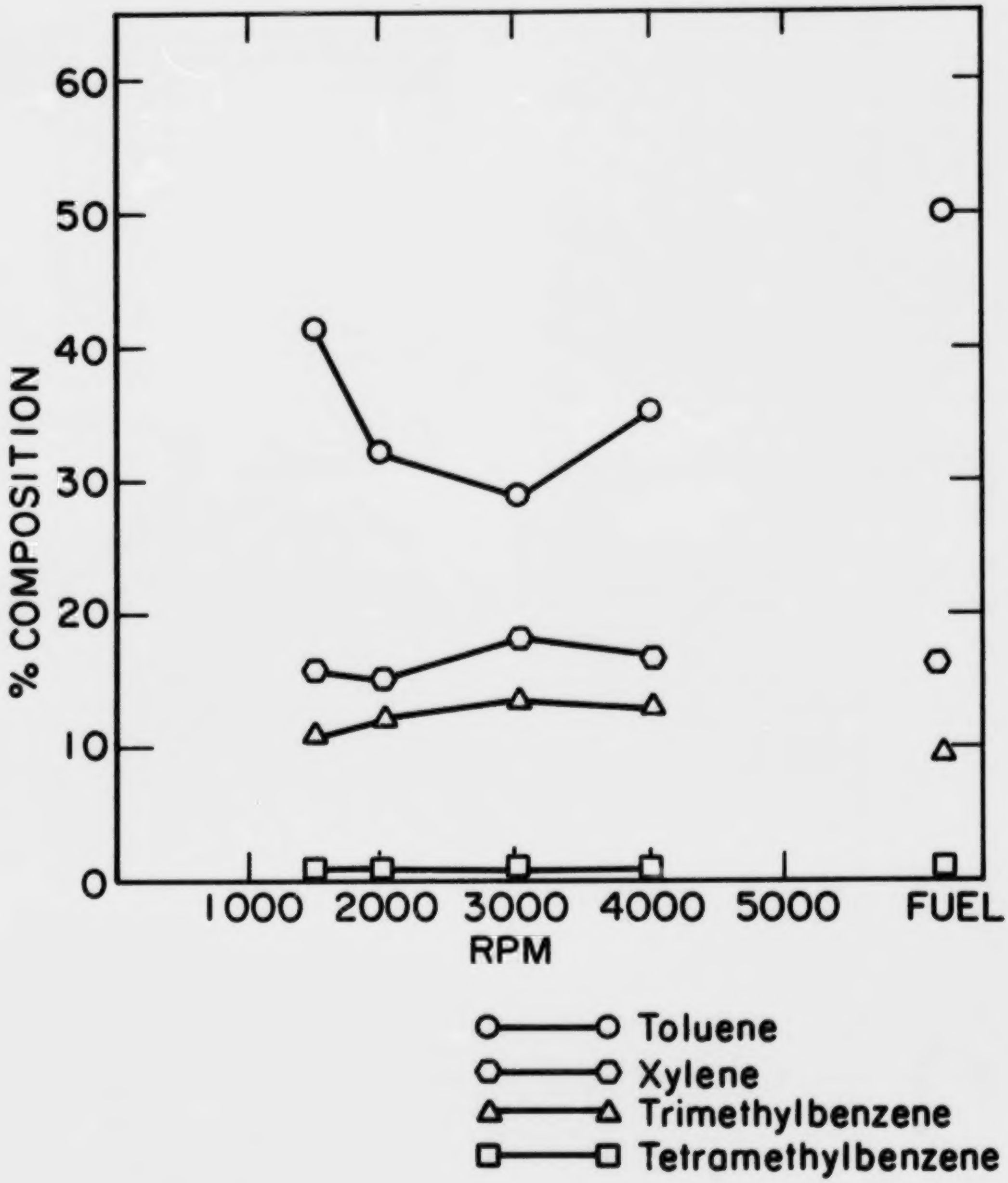


Figure 46 Aromatic Composition from Mercury 50 HP.

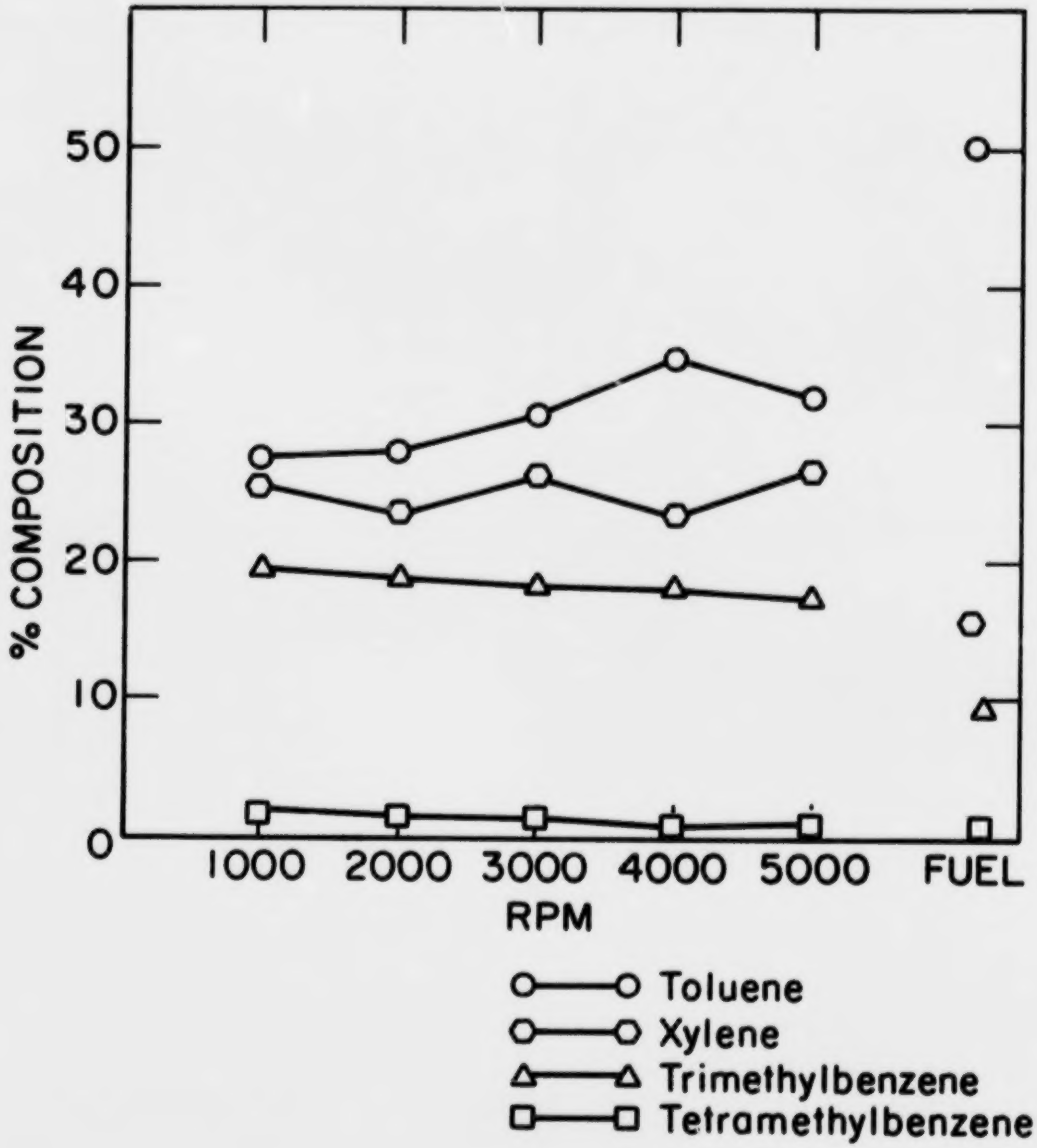


Figure 47 Aromatic Composition from Chrysler 105 HP.

randomly selected samples of the condensable fraction. In particular, naphthalene and its two isomeric methyl derivatives were identified by comparison of their retention times with those of the pure compounds. A typical gas chromatogram is shown in Figure 48. In six samples analyzed, the three binuclear aromatics ranged from 1-2% of the total mononuclear aromatic content of the condensate. This level is somewhat higher than that in the raw fuel (0.5% binuclear aromatics).

Olefins

Olefins were determined by amperometric titration using a standard ASTM Method (20). Phenols interfered and were removed by extraction with 0.1 N NaOH. The ASTM procedure yields analytic information in terms of moles of olefin. To calculate the weight of olefin condensed an average molecular weight is needed. It was decided that a reasonable manner in which to calculate this number was to assume that the olefin distribution in the condensate was -- to a first approximation -- the same as that in the fuel. The latter had an average molecular weight of 86. Olefins, therefore, are reported as cyclohexene (molecular weight 82).

Phenols

Phenols were determined on the base extract from the

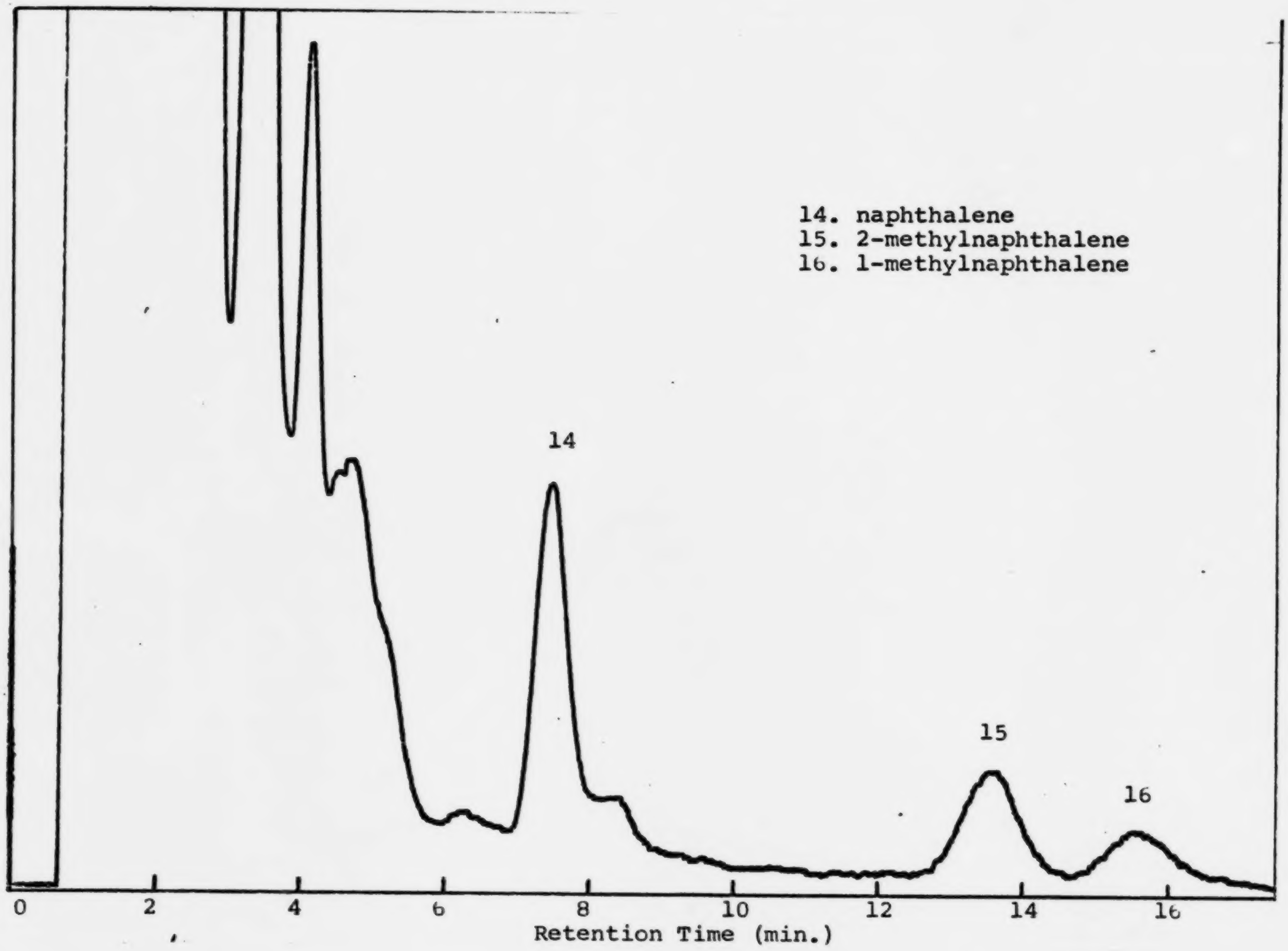


Figure 48 Typical Gas Chromatogram of Outboard Engine Exhaust Condensate. (Solvent: $CHCl_3$. Analytical Conditions: PMPE column at 125°C; He flow rate 30 ml/min.)

olefin determination by ultraviolet spectroscopy. Due to the high background absorbance, however, it was necessary to take the difference in absorbance at 290 millimicrons between an acidic and basic solution (21, 22). Typical spectra are shown in Figures 49 and 50.

Carbonyl Compounds

Carbonyl compounds were determined by direct infrared spectroscopy on the organic phase of the extracted condensate (23-25). No attempt was made to distinguish between the various types of carbonyl compounds; the peak at about 5.9 microns was measured and compared with known solutions of butyraldehyde. Base extraction lowered the absorbance in a random selection of samples by 7-12%, indicating an acid content of roughly 1/10 of the carbonyl signal.

Paraffinic Hydrocarbons

Paraffinic hydrocarbons were not determined directly; however, paraffins could be estimated by obtaining the total condensable hydrocarbons, subtracting the major constituents (olefins and aromatics) and assuming the remainder to be paraffins. Such a procedure is discussed in the following section.

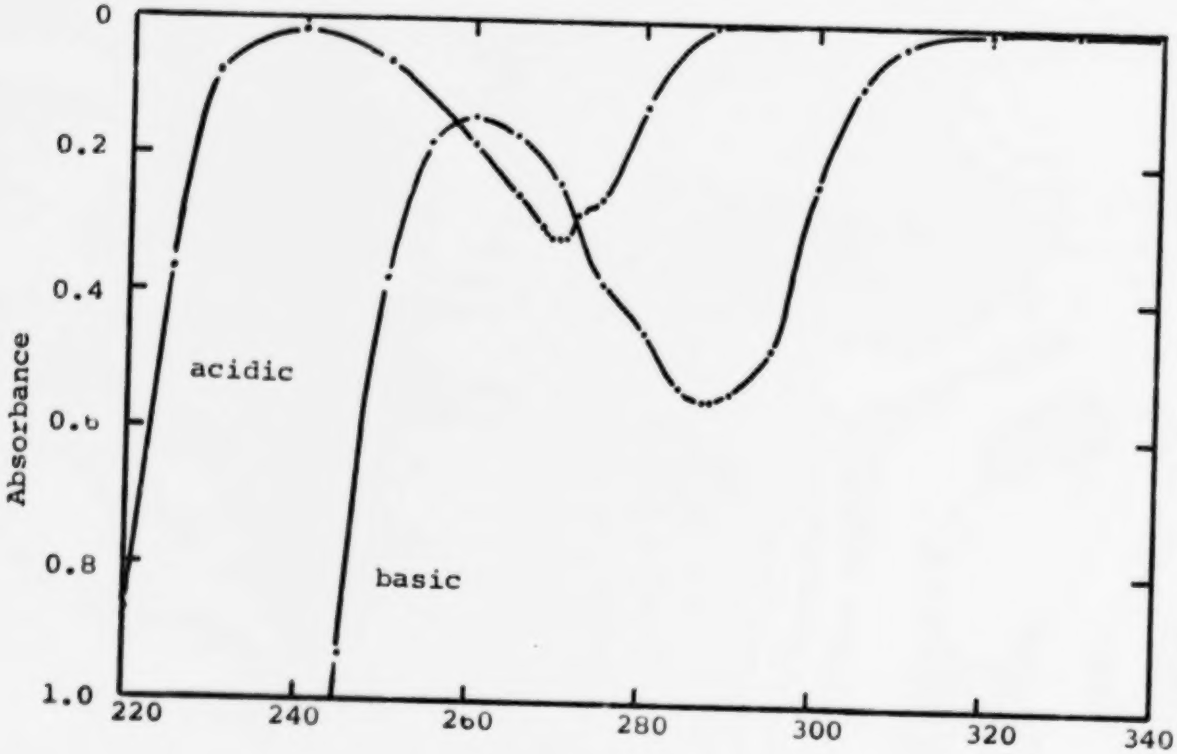
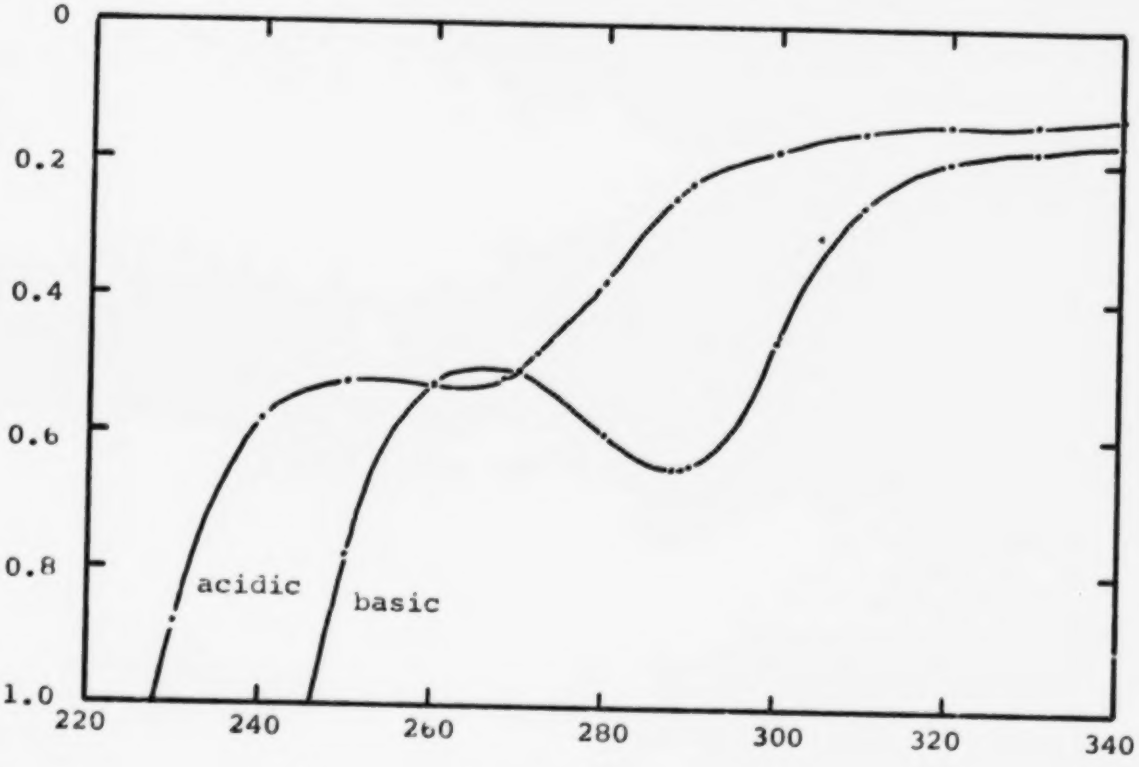


Figure 49. Ultraviolet Absorbance Spectrum of Phenol in Basic and Acidic Solutions



Wavelength (mu)

Figure 50. Ultraviolet Absorbance Spectrum of NaOH Extract and Acidified NaOH Extract of Typical Condensate Sample

Determination of Organic Material and Water in a Condensate Sample

Determination of the total amount of organic material condensed from the exhaust is complicated by the fact that considerable water is formed during the combustion process and condensed in the traps. For one particular engine, the normal addition of $CHCl_3$ to the condensate was eliminated.

Receivers on both the first and second stage condensation stages were tared. After the engine test had been run, the receivers were allowed to come to room temperature and weighed. The condensates consisted of a two phase mixture of organic material and water. Tetrahydrofuran was added to each condensate until a single phase was obtained and the total weight obtained. Aliquots of the solution were titrated for water content by a standard Karl Fisher titration. The moisture content of the tetrahydrofuran was determined in a separate titration and this blank subtracted from the value obtained on the condensate. The organic content was then calculated as the total weight of condensate minus the weight of water. Results are presented in Table 9.

RESULTS AND DISCUSSION

Condensables concentration was measured in duplicate runs for the first few engines tested. Reproducibility was

Table 9. Condensable Material in Each Stage as Water and Organic Material (Chrysler 3.6 hp Engine)

Sample	Total Wt. (g)	Total Organics (g)	% Organics	% of Total Condensable Organics
1000 r.p.m.				
Stage I (1-3°C)	34.52	0.47	1.4	18
Stage II (-65°C)	3.97	2.18	55.0	82
2000 r.p.m.				
Stage I (1-3°C)	15.68	0.50	3.2	19
Stage II (-65°C)	3.58	2.16	60.5	81
3000 r.p.m.				
Stage I (1-3°C)	16.12	0.43	2.6	24
Stage II (-65°C)	2.81	1.34	47.7	76

very good, and it was decided that single condensate collections would suffice thereafter. Most of the data presented, therefore, is based on single engine runs.

Results of the exhaust condensate analysis are presented in Table 10. The last two columns entitled Total Condensable Mononuclear Aromatics were calculated as follows: the TCMA quantity in grams/hr was calculated by multiplying the observed condensable mononuclear aromatics in mg/cu ft. by the total exhaust in cu ft./hr and dividing by 1000 to convert mg to grams; the TCMA quantity in grams/kg was calculated by dividing the grams/hr. value by the fuel consumption rate (kg/hr) to give grams of condensable mononuclear aromatic per kg. of fuel.

There seemed to be no trend in the condensable aromatic concentration of the exhaust with engine size, as shown in Figure 51. There did seem to be a minimum for all engines in the middle range (2000-3000 rpm). This is to be expected since the engines are designed to operate at maximum efficiency in this range. Additionally, the concentration of condensable aromatic hydrocarbons did not differ significantly when drained and undrained engines were compared (Figure 52).

The results of the family composition determination for the 3.6 hp Chrysler engine are presented graphically in Figure 53. The data shows that the composition of the condensate does not vary greatly with engine speed and closely approximates the family composition of the fuel. As can be

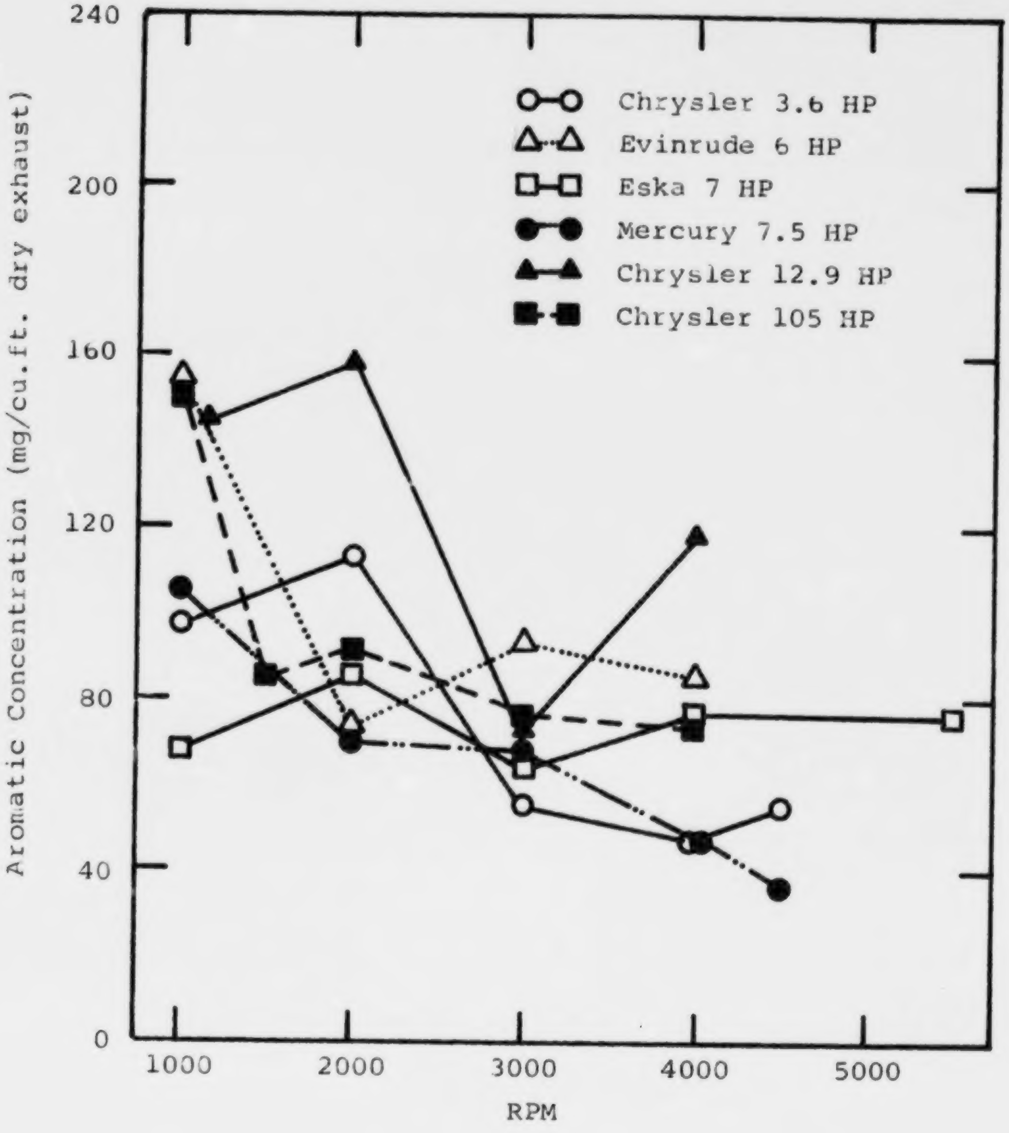


Figure 51 Mononuclear Aromatic Concentration in the Condensable Exhaust from Six Outboard Engines vs. RPM

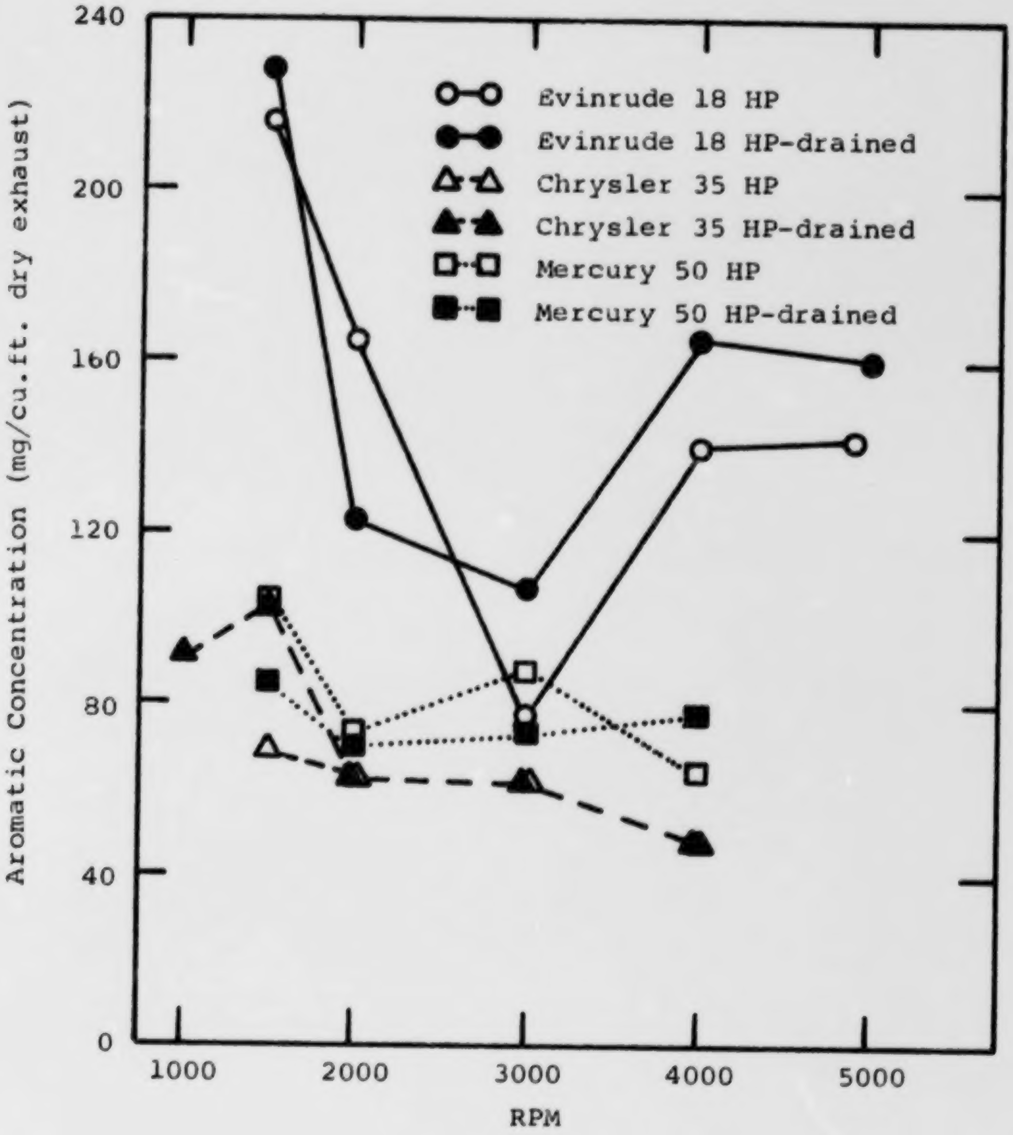


Figure 52 Comparison of Monocuclear Aromatic Concentration in the Condensable Exhaust for Drained and Undrained Outboard Engines

TABLE 10

SUMMARY OF CONDENSATE ANALYSES

Engine and Speed (RPM)	Fuel Consumption Rate (kg/hr.)	Total Exhaust (cu.ft./ hr.)	Concentrations of Condensable Substances: (mg/cu.ft.) Mononuclear Aromatic	Olefin*	Phenol*	Carbonyl*	Total Condensable Mononuclear Aromatics (g/hr.)	(g/kg fuel)
Chrysler 3.6 hp (air-cooled)								
1000	0.322	111	98	18.0	-	-	10.9	33.9
2000	0.589	190	113	20.3	-	-	21.5	36.5
3000	0.815	281	55	15.3	-	-	15.5	19.0
4000	1.060	407	47	10.2	1.53	10.8	19.1	18.0
4500	1.287	482	55	10.3	1.26	10.2	26.5	20.6
Evinrude 6 hp								
1000	0.392	148	155	-	-	8.8	22.9	58.4
2000	0.835	305	74	-	-	8.8	22.6	27.1
3000	1.593	554	85	-	-	11.0	47.1	29.6
4000	2.447	948	85	-	1.53	12.7	80.6	32.9
Eska 7 hp (air-cooled)								
1000	0.284	107	69	11.3	0.90	7.8	7.4	25.7
2000	0.528	194	86	17.7	1.05	11.5	16.7	31.5
3000	0.912	294	64	13.0	0.72	9.0	18.8	20.7
4000	1.361	453	76	13.5	0.63	6.8	34.4	25.3
5500	2.409	827	76	10.5	0.82	5.3	62.9	26.0
Mercury 7.5 hp								
1000	0.5559	205	105	19.3	-	7.0	21.5	38.5
2000	1.074	383	70	14.1	-	5.8	26.8	25.0
3000	1.628	849	68	-	-	6.8	57.7	35.4
4000	2.220	905	36	-	-	7.2	32.6	14.7
Chrysler 12.9 hp								
1150	0.900	313	145	18.8	1.15	9.5	45.4	50.4
2000	1.432	495	159	19.2	1.07	14.5	78.7	55.0
3000	1.770	656	73	11.6	1.57	9.5	47.9	27.1
4000	2.952	1070	119	15.0	1.82	18.3	127	43.0
5000	4.298	1575	132	17.2	3.37	12.5	208	48.4

TABLE 10 (Cont'd)

SUMMARY OF CONDENSATE ANALYSES

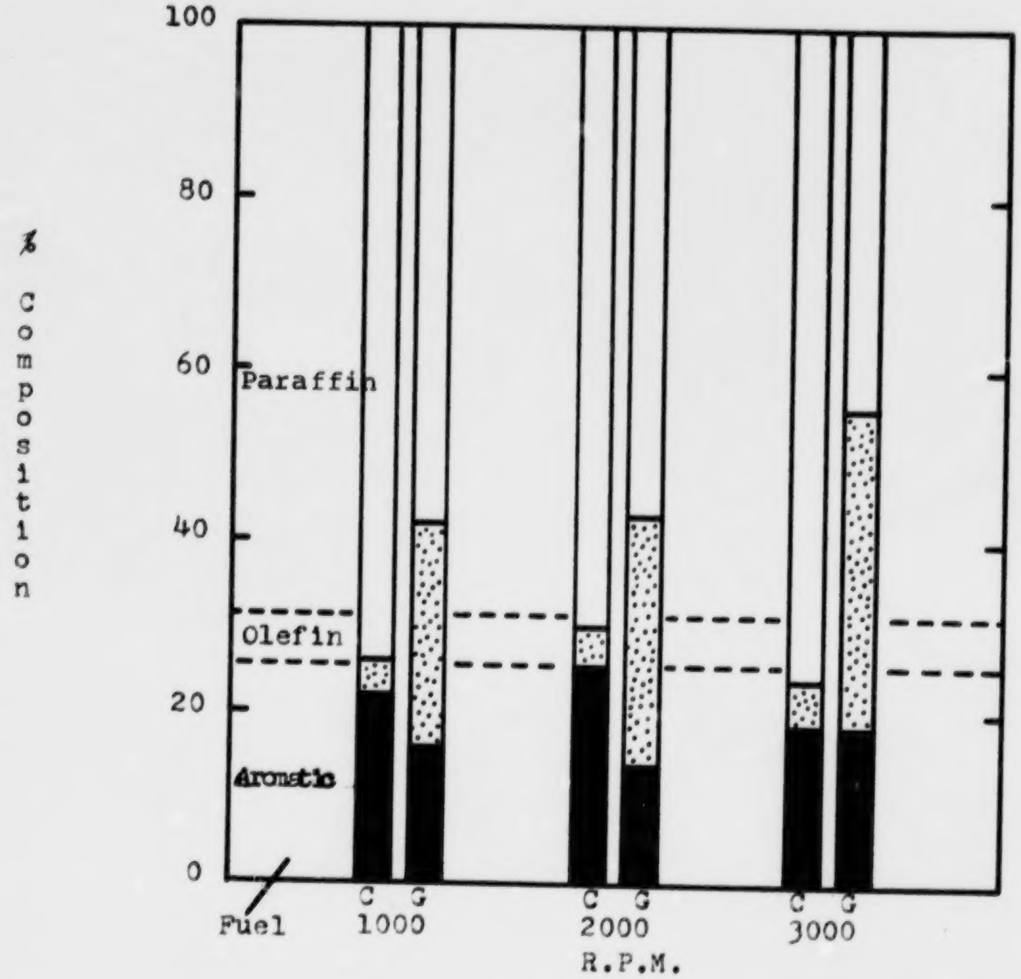
Engine and Speed (RPM)	Fuel Consumption Rate (kg/hr.)	Total Exhaust (cu.ft./hr.)	Concentrations of Condensable Substances: (mg/cu.ft.)				Total Condensable Mononuclear Aromatics	
			Mononuclear Aromatic	Olefin*	Phenol*	Carbonyl*	(g/hr.)	(g/kg fuel)
Evinrude 18 hp								
1500	1.821	599	217	36.0	4.70	-	130	71.4
2000	2.400	810	165	13.7	1.65	11.8	134	55.8
3000	3.740	1220	77	13.0	1.43	12.5	93.9	25.1
4000	5.249	1818	140	15.8	1.80	-	255	48.6
4900	7.398	2478	142	12.0	1.05	19.5	352	47.6
Evinrude 18 hp - drained								
1500	1.724	581	229	20.3	1.48	26.8	133	44.8
2000	1.926	692	123	17.3	2.08	30.0	85.1	44.2
3000	3.049	1064	107	17.6	1.92	14.0	114	37.4
4000	5.873	1905	165	17.3	1.08	13.3	314	53.5
5000	6.783	2347	160	16.3	0.80	9.8	376	55.4
Chrysler 35 hp								
1500	2.509	873	69	-	1.93	10.5	60.2	24.0
2000	3.502	1290	63	-	3.56	8.8	81.3	23.2
3000	7.447	2381	61	-	-	8.7	145	19.5
4000	8.900	3401	48	11.6	1.80	11.0	163	18.3
Chrysler 35 hp - drained								
1000	2.440	822	92	-	-	9.3	75	30.9
1500	3.554	1211	103	16.7	1.05	8.8	125	35.2
2000	4.015	1366	63	-	-	8.8	85	21.3
3000	6.319	2331	61	-	-	12.8	142	22.4
4000	9.380	3490	48	-	-	12.7	169	18.0
Mercury 50 hp								
1500	3.477	1266	104	14.2	0.53	6.7	132	38.0
2000	3.540	1370	73	9.8	0.80	7.3	100	28.2
3000	6.581	2326	88	9.3	0.52	5.2	205	31.2
4000	9.828	3643	63	7.3	0.52	6.5	230	23.4

TABLE 10 (Cont'd)

SUMMARY OF CONDENSATE ANALYSES

Engine and Speed (RPM)	Fuel Consumption Rate (kg/hr.)	Total Exhaust (cu.ft./hr.)	Concentrations of Condensable Substances: (mg/cu.ft.)				Total Condensable Mononuclear Aromatics	
			Mononuclear Aromatic	Olefin*	Phenol*	Carbonyl*	(g/hr.)	(g/kg fuel)
Mercury 50 hp - drained								
1500	3.779	1376	85	-	-	5.8	117	31.0
2000	3.784	1460	70	-	-	6.8	102	27.0
3000	6.787	2404	73	-	-	5.5	175	25.8
4000	10.390	3824	78	-	-	7.7	298	28.7
Chrysler 105 hp								
1000	4.472	1550	150	20.0	-	28.6	233	52.1
1500	5.655	2094	86	19.7	-	19.0	180	31.8
2000	6.557	2513	91	19.5	2.05	62.2	188	28.7
3000	9.666	3663	76	14.5	1.85	66.0	278	28.7
4000	16.636	6369	74	16.5	-	29.3	467	28.1
Chrysler 35 hp (field engine - new plugs)								
1500	2.532	855	90	-	-	6.7	77	30.4
2000	3.333	1093	64	-	-	4.9	70	21.0
3000	7.217	2205	78	-	-	4.4	172	23.8
4000	9.289	3344	77	-	-	6.5	257	27.7
Evinrude 18 hp (field engine as received)								
1000	1.460	475	123	-	-	8.8	58.4	40.0
2000	2.195	760	56	-	-	8.1	42.6	19.4
3000	3.493	1163	45	-	-	7.2	52.3	15.0
4000	5.073	1802	43	-	-	9.0	77.5	15.3
Evinrude 18 hp (field engine new plugs)								
1500	1.870	-	71	-	-	7.2	-	-
2000	2.140	736	73	-	-	10.1	53.7	25.1
3000	3.695	1247	49	-	-	7.8	61.1	16.5
4000	5.073	-	40	-	-	7.8	-	-
4500	7.000	-	45	-	-	6.4	-	-

* Olefin expressed as cyclohexene; phenol as p-cresol; carbonyl as butyraldehyde



C = Condensate analysis
G = Gas stream analysis
Order from bottom = aromatic, olefin, paraffin

Figure 53 Composition by Hydrocarbon Families of Condensate and of Exhaust Gas Stream, Superimposed over that of Raw Fuel. Engine: Chyrsler 3.6 HP

seen as well, this is not true of the total exhaust stream. In particular, there would seem to be non-condensable olefins produced from the paraffinic and aromatic portions of the fuel, probably largely ethylene andpropylene. This restructuring was observed for gaseous emissions (vide supra), but it should be noted here that the phonemenon apparently has little effect on condensables and therefore little significance relative to inputs to the aquatic environment.

The results presented in Table 9 show that, for this engine, some interesting trends emerge. The greatest part of the material trapped in the ice water condenser consisted of water, with organics amounting to only about 1.5-3%. This amount of condensable organics amounted to 18-24% of the total condensate. Much less material is condensed in the dry-ice cooled trap, but the material is much richer in organics. This is to be expected since the water content of the exhaust stream is substantially reduced by the ice-water condenser. If the case can be made that this engine can be considered average with respect to exhaust emissions relative to all engines tested, then it is possible to estimate that amount of the fuel fed to the engine which could be expected to be condensed in the water column. The argument for considering the data obtained for this engine as representative for all engines is twofold. First, although the family composition of the total exhaust varied widely, the condensate family composition ramined farily constant; further, the range of compositions encountered for this engine encompassed almost exactly the range of composition encountered for the largest engine (105 hp) as shown in Figure 19. Additionally, the total condensable aromatics listed in Table 10 for this engine appears to be average for all engines.

Therefore, one can convert total condensable aromatics to total condensable hydrocarbons by multiplying by 4 or 5 (20-25% of the condensate is aromatic). Then, assuming that the ice-water condenser most closely approximates the condensation conditions in a lake, one can apply the data from Table 9, which shows that 18-24% of the condensable organics are found in the first stage condenser. One would, therefore, divide the total condensable hydrocarbons by about 4 or 5 to obtain hydrocarbons condensable at 1-3°C. The outcome of these two operations, which cancel fortuitously, is that total condensable aromatics very nearly equal water column condensable hydrocarbons.

If 3000 rpm is selected as the speed at which most boat usage occurs, and the values of total condensable aromatics as percent of fuel is averaged over all engines tested in this study, a figure of 2.5% condensable aromatics is obtained. Since by previous argument this figure is close to the value for total condensable hydrocarbons in a lake usage situation, the conclusion may be reached that the "average" engine will contribute about 2.5% of its fuel to the water, exclusive of drainage, during most of the time it is in use. The range of values encountered is 1.5-7% for all engines at all speeds. These values are lower than those found in the literature (4), due largely to the failure on the part of previous estimates to take condensability into account (4,5).

SECTION VI

EVAPORATION OF CONDENSED OUTBOARD ENGINE EMISSIONS FROM THE WATER COLUMN

INTRODUCTION

Several mechanisms are operative in removing hydrocarbons and hydrocarbon-derived products from outboard engines from the aquatic environment. Most significant of these are biodegradation, adsorption onto colloidal material and subsequent transport to the sediment, and evaporation. Only the last, evaporation, was evaluated in this study due to project scope and time constraints. It is recognized, however, that the other two pathways are areas for further investigation. Some estimation of the effects of these other phenomena can be derived from data from the field studies, in which productivity and hydrocarbon content of the sediment were examined.

Evaporation is essentially a gas-transfer process, the rate of which is expected to exhibit a first-order dependence on solution-phase concentration of the evaporating substance and to be additionally dependent on the surface area to volume ratio, the rate of transport of material from bulk solution to the phase interface or surface, and temperature (26). In a truly quiescent system, bulk transport proceeds by diffusion alone, and in a stirred system by both diffusion and convection. Overall transport phenomena in a natural system are difficult to quantify and simulate experimentally. Nonetheless, diffusion-controlled transport under quiescent conditions should represent the lower limit on evaporation rate, all other parameters being the same.

Aromatics were chosen as the class of materials for evaluation in the evaporation studies; primarily because, as previously mentioned, they are the most toxic of the components of the fuel, but additionally because their concentration is more easily measured, especially at low concentrations.

EXPERIMENTAL PROCEDURE

The effect of each of the parameters affecting evaporation rate was studied by varying one at a time while holding all others constant. Concentrations of both model aromatic compounds and "OME water" (the single phase mixture of water and hydrocarbons resulting from running a small outboard engine in a 55-gallon drum of water for a short period) were monitored by ultraviolet absorbance measurements. The reactor utilized for the evaporation rate studies is illustrated schematically in Figure 54.

RESULTS AND DISCUSSION

Preliminary Investigation

The evaporation of both single mononuclear aromatic components and of OME water was measured under both quiescent and completely mixed conditions. The results are shown in Figures 55 and 56. For the experiment described by the data presented in Figure 55, mixing was provided by introduction of air through a diffuser at the bottom of the reactor. As expected, the effect of mixing is to increase the rate of evaporation. However, an important observation can be drawn from the data, namely that outboard engine exhaust products in water decay to a non-zero value, in contrast to a pure, single-component system. The fraction of the total signal remaining is variable since it depends on the length of time for which the engine was run. The data does show that there is an aromatic-containing constituent of the exhaust products, which is removed only very slowly from the aquatic system by evaporation. The presence of napthalenes detected in the condensate (see p. 97) does not explain the observed effect since these should have a half-life for evaporation from a completely mixed system of 1 meter depth of about 3 hours (27).

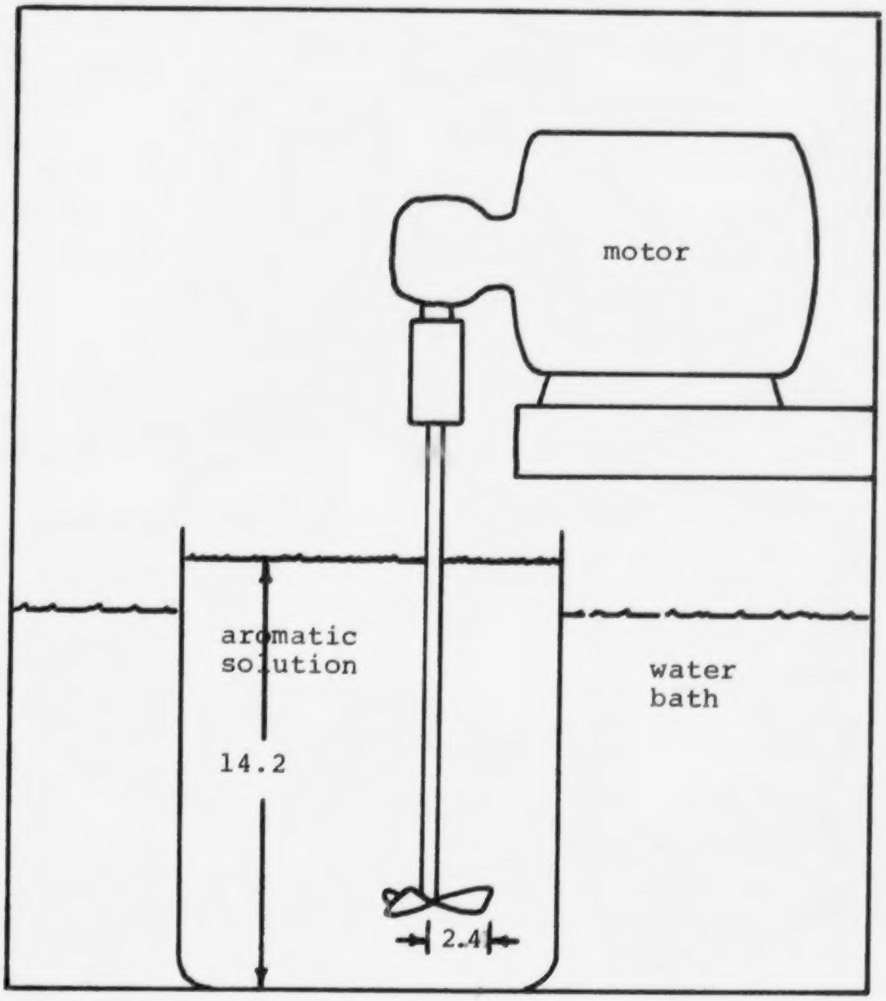

motor
aromatic solution
water bath
14.2
2.4

Figure 54 Evaporation Apparatus with Temperature Control and Turbulence Supply

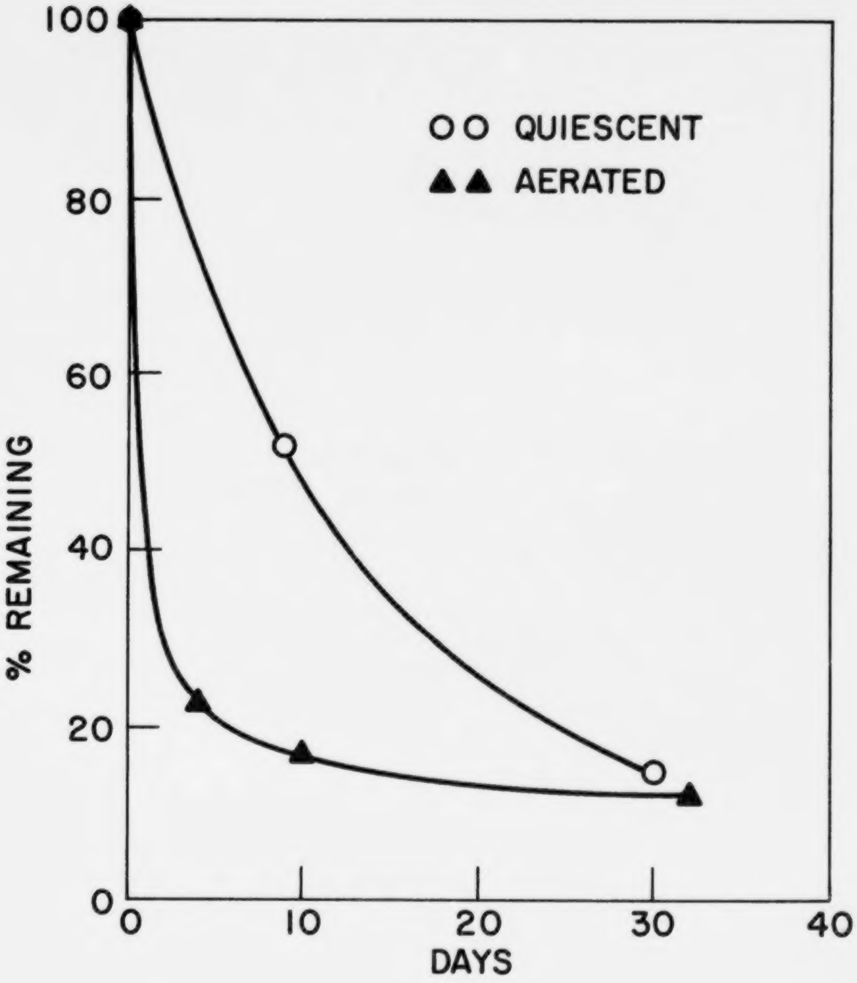


Fig. 55 DISAPPEARENCE OF OUTBOARD ENGINE EXHAUST PRODUCTS FROM AERATED AND QUIESCENT AQUEOUS SYSTEMS AT ROOM TEMPERATURE.

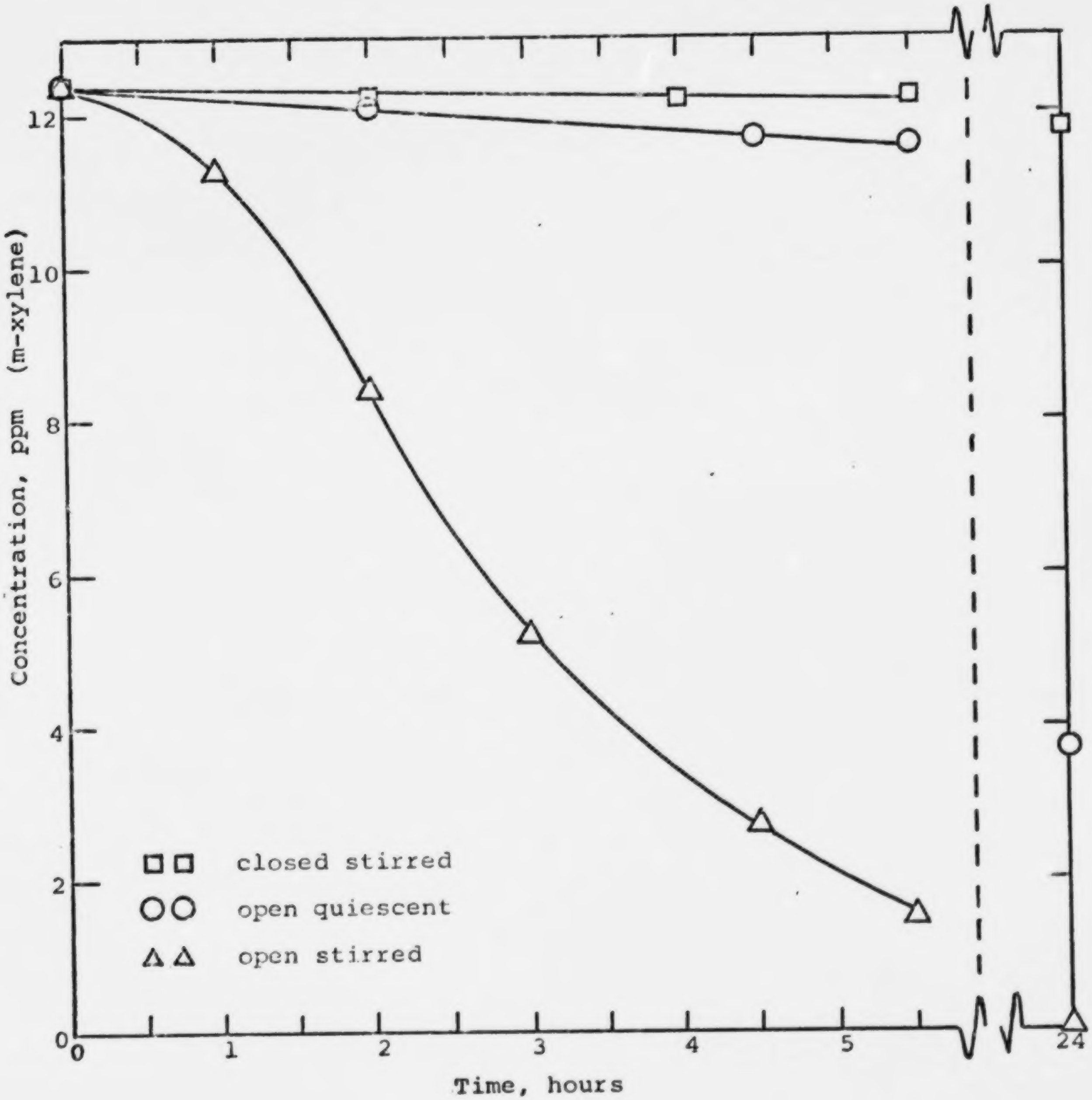


Figure 56 Evaporation of m-xylene in Quiescent (open circles) and stirred (open triangles) Aqueous Systems at pH 8.3 (0.1 N $NaHCO_3$) and at 22 ± 1 deg. C.

Our results indicate a much longer half-life for the condensate materials. This longer half-life suggests either that the material is very water soluble, which is unlikely, or that its vapor pressure is very low for reasons of very high molecular weight, which seems most likely. This would strongly suggest that the source of the material in question is the oil fraction of the fuel mixture. In subsequent experiments rates of disappearance of aromatic species refer only to that fraction of such species which are volatile under the experimental conditions.

Reaction Order

To verify that the concentration dependence of evaporation is first order, various concentrations of toluene in water were prepared and their disappearance studied under completely mixed conditions in the stirred reactor shown in Figure 54. Experimental conditions were as follows:

Concentration: varied from 1.43 to 57.2 ppm (vol)
Stirring: 100 rpm
Temperature: 23.5±0.5 °C

Results shown in Figure 57 illustrate that log c versus t is linear and that the reaction is therefore first order in concentration.

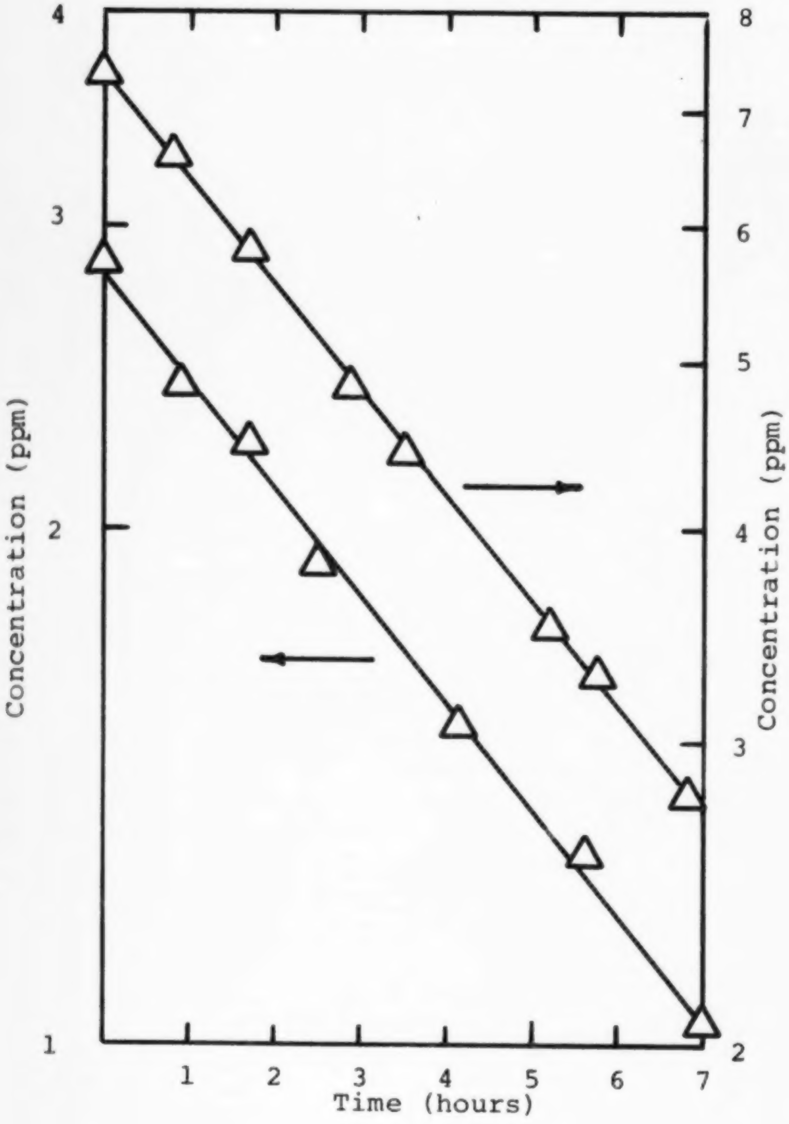


Figure 57 Toulene Concentration Plotted Logarithmically for Two Representative 100 RPM Evaporation Runs

Effect of Stirring

Stirring is expected to affect rate of evaporation in two ways; first by increasing the flux of material from the bulk to the surface, and, secondly, by increasing the surface to volume ratio if, as was true for these experiments, mixing is sufficient to extend into the turbulent range. Experimental conditions were:

Stirring: 0-100 rpm
Temperature: 23.5±0.5 °C
Depth (rest): 0.142 m

Results are shown in Figure 58. Although there is considerable scatter, especially as turbulence increases, the increase in the rate coefficient with stirring is clearly evident for the cases of both pure toluene and OME water.

The Effect of Surface to Volume Ratio

The effect of the surface to volume ratio (S/V) was demonstrated by varying the depth of the liquid phase (S/V = 1/D). Conditions were:

Depth: .0425 to 0.172 m
Stirring: none
Temperature: 24.5±0.5 °C

Results presented in Figure 59 show the anticipated result that the rate coefficient is inversely proportional to depth.

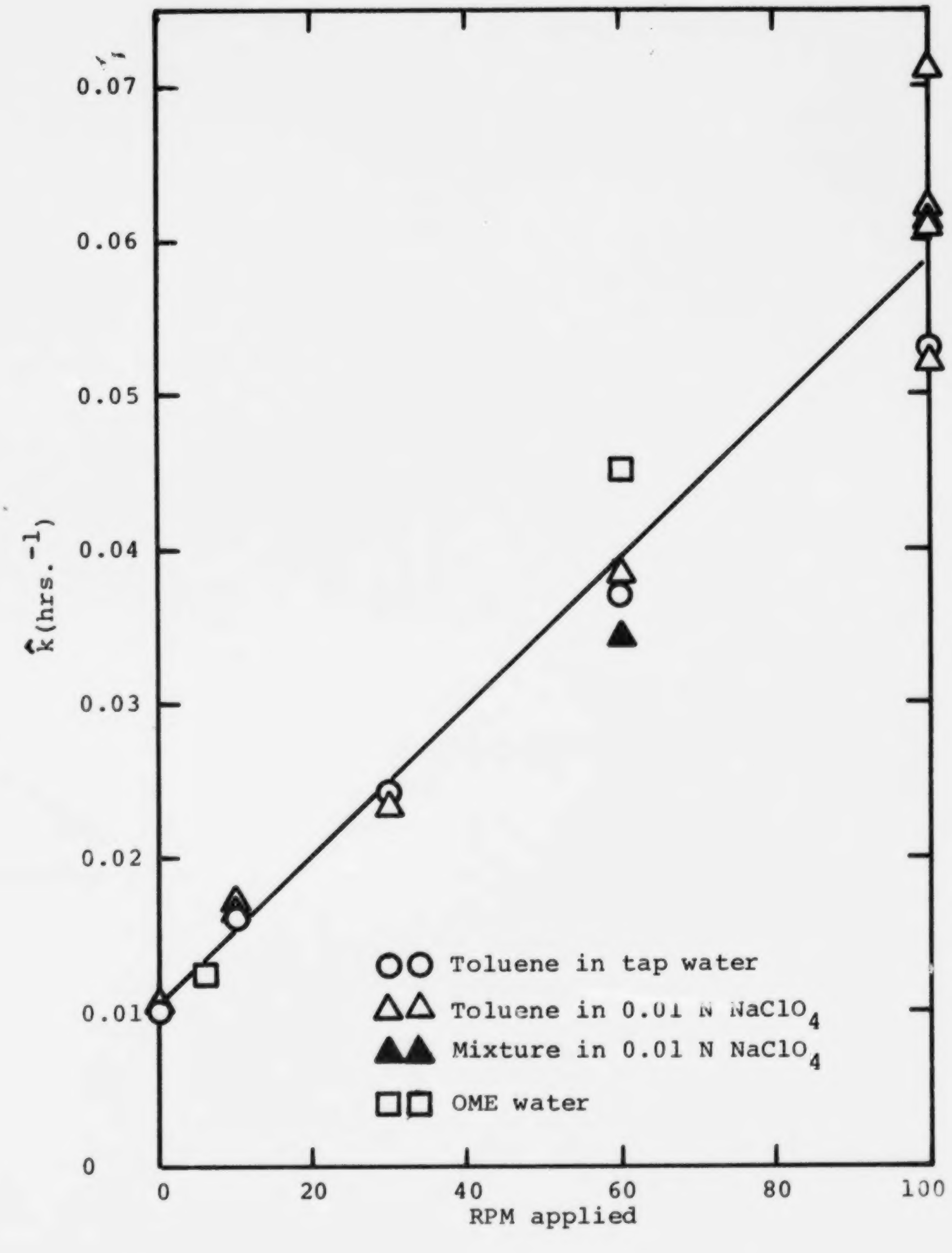


Figure 58 Evaporation Rate Coefficient Dependency on Stirring

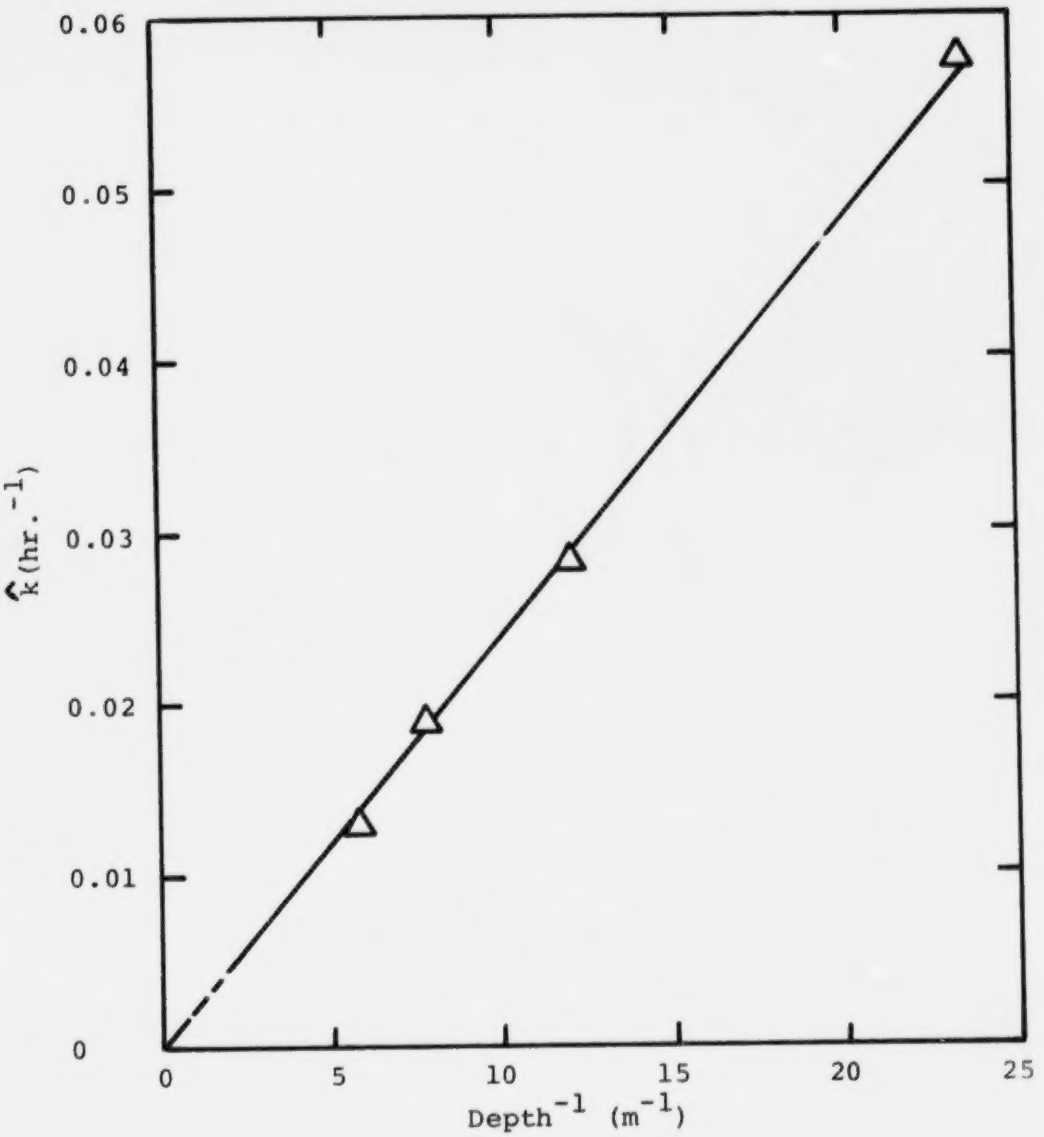


Figure 59 Evaporation Rate Coefficient Dependency on Depth or Surface Volume Ratio (1/D = S/V)

The Effect of Temperature

The change in rate with temperature for a chemical reaction or change of state is governed by the Arrhenius equation, the integrated form of which is

$$\ln k = \frac{Ea}{RT} + \ln A \qquad (1)$$

where Ea is the activation energy and A the so-called frequency factor. For data which may be described by this equation, a plot of ln k versus 1/T will yield a linear trace, with a slope of Ea/R and an intercept of ln A. The experimental data plotted in Figure 60 exhibit such behavior. The fact that toluene and OME water fall on the same line is probably trivially related to the facts that: 1) the largest single aromatic component of OME water is toluene; and, 2) the heats of vaporization for the other major mononuclear aromatics are probably very close to that of toluene.

Experimental conditions were:
Temperature: 10.0 to 43.7 °C
Stirring: none
Depth: 0.142 m

The Arrhenius equation fitting this data is:

$$\log k = -3.05 \times 10^3 \frac{1}{T} + 7.46 \qquad (2)$$

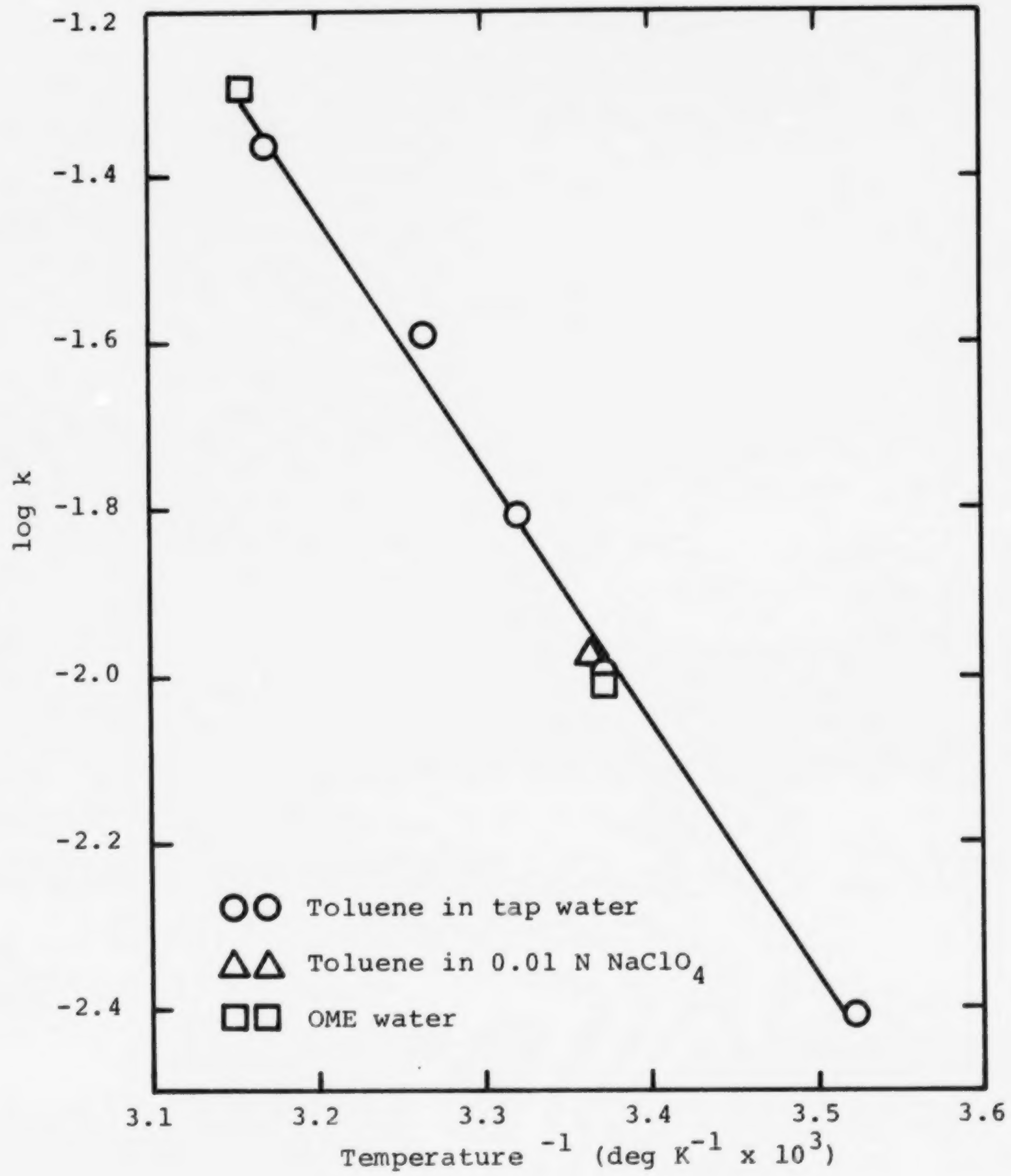


Figure 60 Evaporation Rate Constant Dependency on Temperature

Thus for a chemically homogeneous quiescent stratum of water 1 meter deep, half-lives for OME water are, for various temperatures:

t(°C)	T(half-life)
10	26 days
15	17 days
20	11 days

The evaporation studies show that for a system at rest at constant temperature,

$$\frac{-dC}{dt} = \hat{k}\,\frac{S}{V}\,C \qquad (3)$$

where: C = concentration of mononuclear aromatic;

S/V = surface to volume ratio; and,

$\hat{k}$ = rate coefficient.

At unit (1 meter) depth for such a system half-lives for evaporation are fairly small. Thus one would expect that in the aqueous environment, evaporation is a significant process determining the instantaneous concentration of exhaust products.

SECTION VII

ANALYTICAL METHODS FOR FIELD STUDIES

INTRODUCTION

In the course of the associated project field tests on the Saline ponds it was necessary to measure levels of hydrocarbons dissolved in the water bodies due to outboard engine usage. Special emphasis was placed on the aromatic fraction, again because these compounds are most closely associated with acute toxicity. The concentration levels of hydrocarbons were expected to be much lower than those encountered in either the engine condensate or evaporation studies, and this was indeed the case. The previous analytical methodology, involving the use of gas chromatography or direct ultraviolet measurement on aqueous solutions, was inadequate for this situation. New Methods, therefore, had to be evaluated. This section deals with experimental findings using these techniques.

CARBON EXTRACTION METHOD

The first method to be tried was the carbon adsorption method, which has been used extensively to concentrate organic materials in water (28). The utility of this method for the particular case of hydrocarbons had to be evaluated.

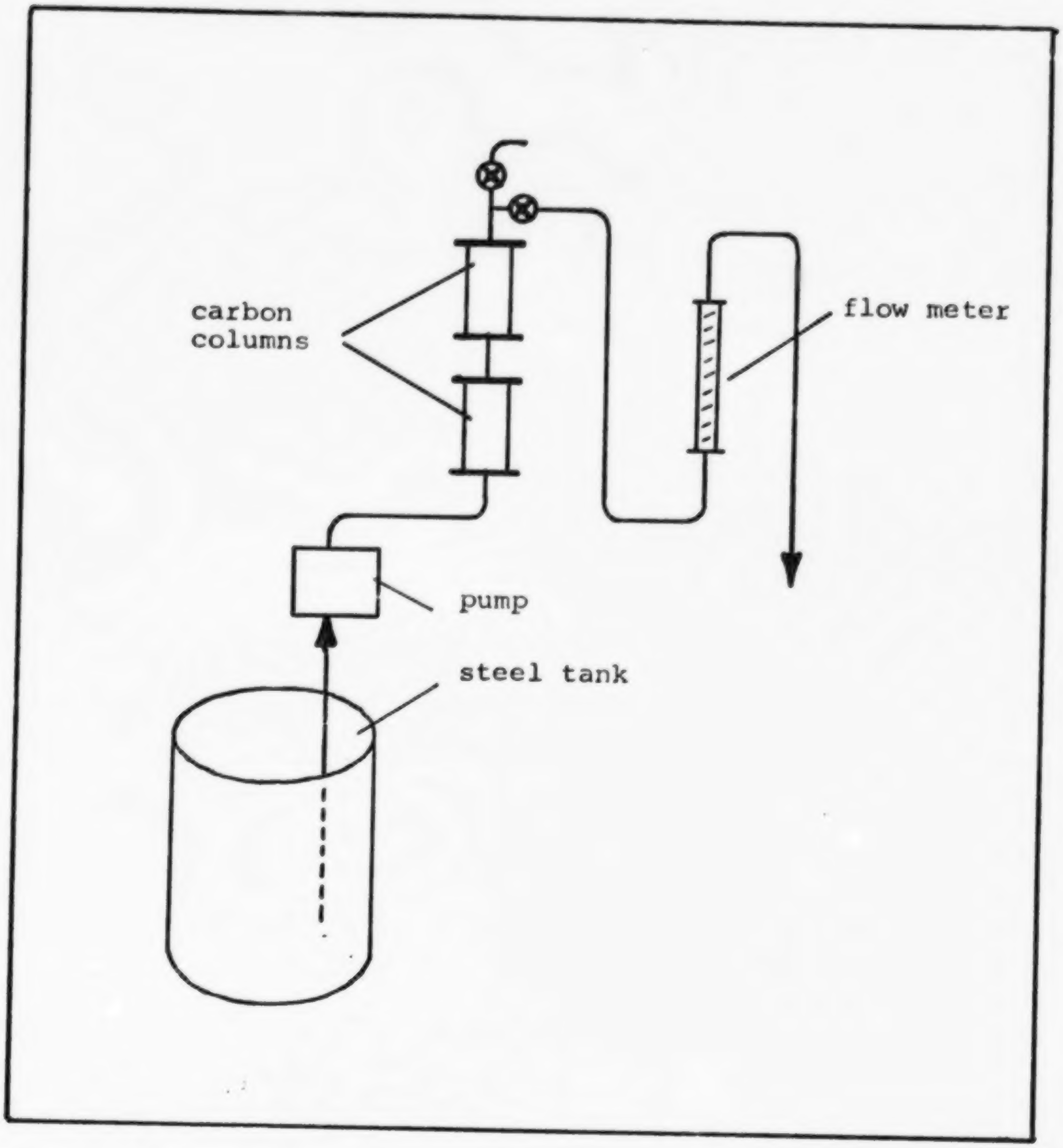

carbon
columns
flow meter
pump
steel tank

Figure 61 Apparatus Used for Activated Carbon Adsorption of Organics from Aqueous Systems

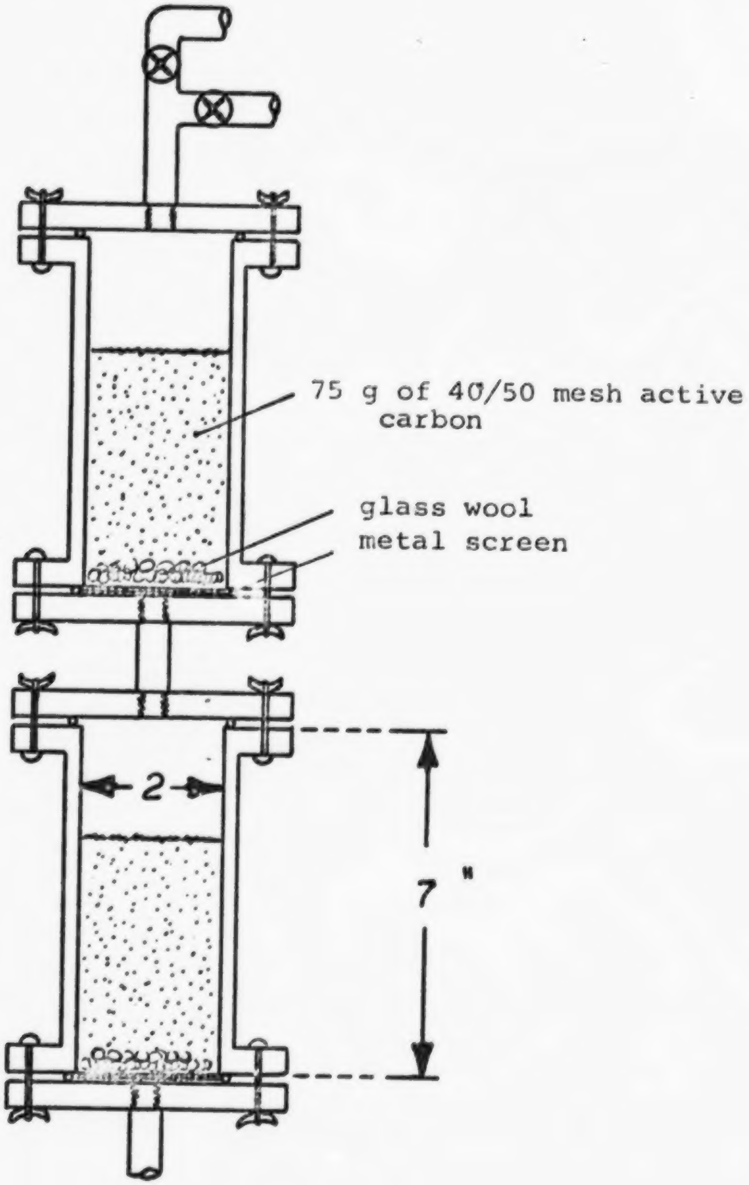

75 g of 40/50 mesh active carbon
glass wool
metal screen
2
7 "

FIGURE 62 Detailed Sketch of Up-Flow Carbon Columns Used in Apparatus Shown in Figure 61. (Columns are constructed with plexiglas.)

Experimental Procedure

A given volume (e.g., 10 or 50 gallons) of "OME water" was pumped by a submersible pump through two upflow columns connected in series each containing 75 g of 40-50 mesh activated carbon. The flow rate through the columns was controlled and measured by a flow meter in series with the columns. The system is shown in Figures 61 and 62. After the chosen volume of "OME water" had passed through the system, the carbon was removed, extracted with chloroform and the organic extract analyzed. Several operational parameters were studied, as described below.

Results and Discussion

Effect of Flow Rate

"OME water" samples were prepared by using 175 ml of Indolene clear gasoline in a 1.5 hp Johnson engine mounted in a 55-gallon tank. A 10-gallon sample of the receiving water was then passed through the adsorbent system at different flow rates. The carbon was air dried at room temperature for about 16 hours and then extracted with 150 ml of chloroform in a Soxhlet extractor for 36 hours. The chloroform extract was then analyzed by gas chromatography using the following conditions:

Column: 3% SE 30 on 100/120 Varaport 30 5' x 1/8" S.S.

Column temperature: 60°C

Carrier gas flow: 30 ml/min He

A typical chromatogram obtained under these conditions is shown in Figure 63. The area under all the peaks was obtained for each flow rate. Results are shown in Table 11.

Figure 64 shows a plot of the first column total peak area versus flow rate from data in Table 11. The strange shape, showing an increase in adsorption with flow rate to a maximum and then a decrease, indicates that effects other than adsorption-desorption were operative. Therefore, work was done to determine the effects of other parameters.

Effects of Air Drying on Extraction Efficiency --

The effect of air drying the carbon before elution with $CHCl_3$ was investigated by running the same material at the same flow rate through the same carbon adsorption system twice and then comparing recoveries by gas chromatography when the adsorbent was dried prior to elution and when it was not dried. The experimental conditions were:

Sample generation:

Engine: 9.5 hp Johnson

Fuel consumption: 1500 ml

Receiving volume: 290 gallons

Adsorption:

Using the apparatus previously described at a flow rate of 500 ml/min through the adsorbers.

Table 11

Effects of Flow Rate on Adsorption of OME Products on Activated Carbon

Flow Rate ml/minute	Time of Flow Minutes	Relative Total Peak Area of Chromatogram	
		First Column	Second Column
217	175	1787	270
291	130	1896	258
367	103	2279	260
485	78	2030	-
533	71	1700	80

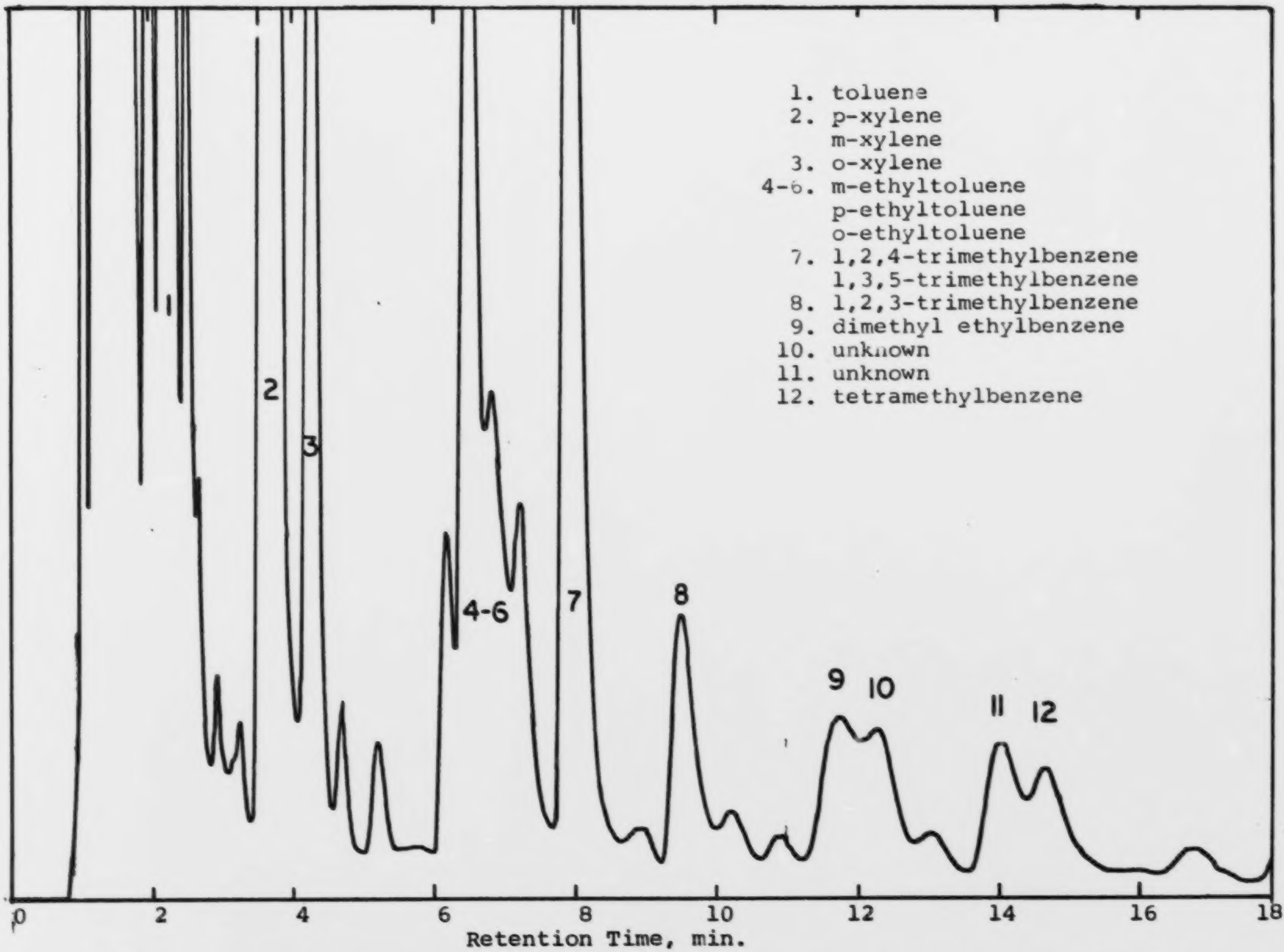


Figure 63 Typical Gas Chromatogram of Outboard Engine Exhaust Products Recovered from Water with Activated Carbon. (Analytical conditions: SE 30 column at 60 degrees C; He flow rate, 30 ml/min.)

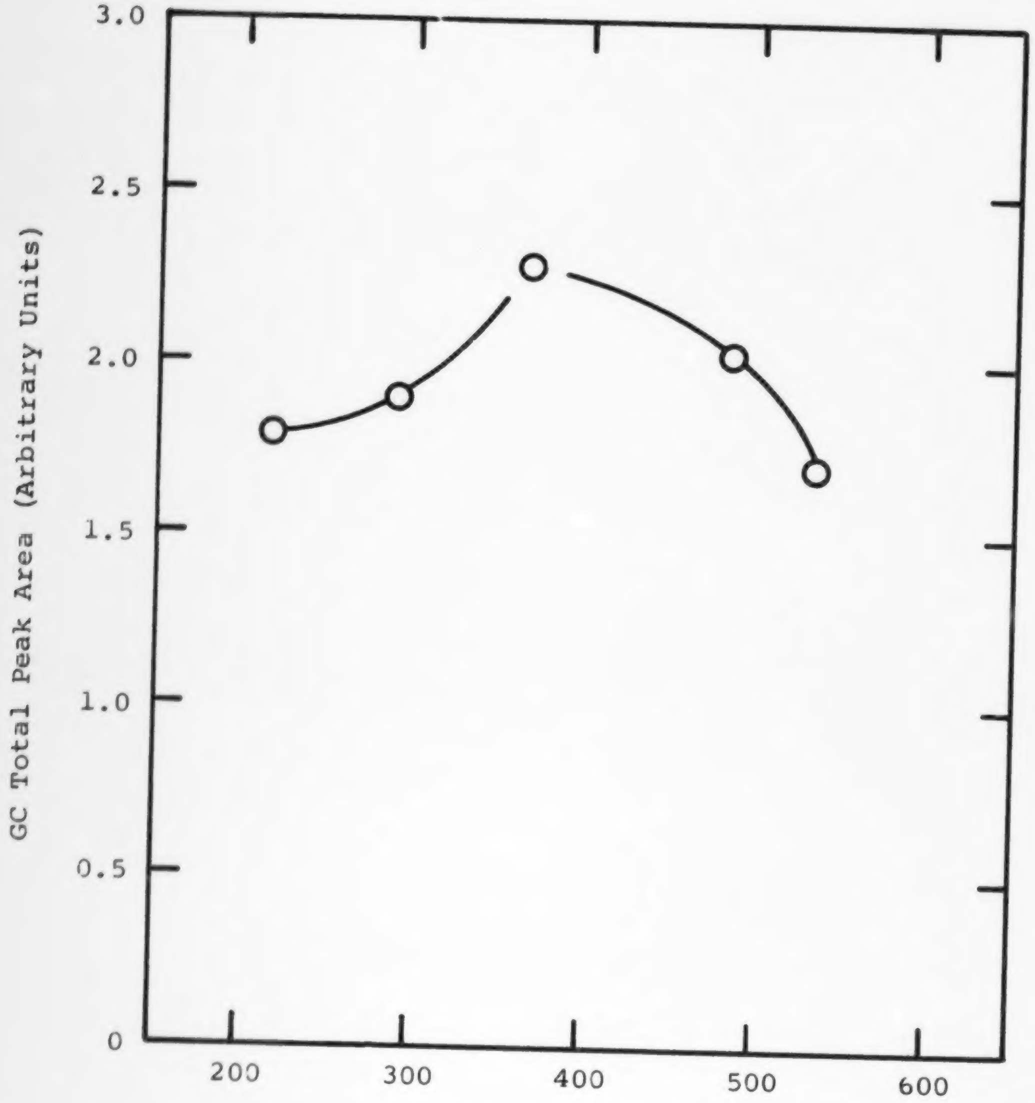


Figure 64 Total Peak Area of All Mononuclear Aromatics Eluted from the First Carbon Adsorption Column versus Flow Rate of Aqueous Solution Through the Adsorbers

Analysis:

Gas chromatography as previously described Results are presented in Table 12. They show that the wet extraction gave a recovery almost 50% higher than the dry. This is presumeably due to evaporative losses from the carbon during drying. In all succeeding work wet extraction was used.

Effect of Elution Time on Recovery --

These experiments were performed by first preparing a toluene in water solution and performing a batch adsorption operation on that solution using activated carbon. The amount adsorbed was then easily calculated as the difference between the initial and final solution concentrations. The carbon was then eluted with $CHCl_3$ in a Soxhlet Extractor and the concentration in the organic phase measured after each extraction cycle. The results are presented graphically in Figure 65, and show that the limiting elution time is reached at about 25 cycles, corresponding to about 5 hours. An elution time of 8 hours was therefore selected as a conservative number for all succeeding runs.

Effect of Flow Rate on Recovery --

Preliminary investigations (Part I of this series) showed

Table 12

Recovery of OME Products for Wet versus Dry Extraction with Chloroform

Peak Designation* No.	Peak Area of Gas Chromatogram (Arbitrary Units)	
	Dry Extraction	Wet Extraction
1	143	153
2	-	-
3	306	387
4-6	553	890
7	86	120
8	49	89
9	53	94
10	46	68
11	5	17
Total	1241	1818

*For peak designations refer to Figure 63

In all studies that follow, the carbon was extracted wet.

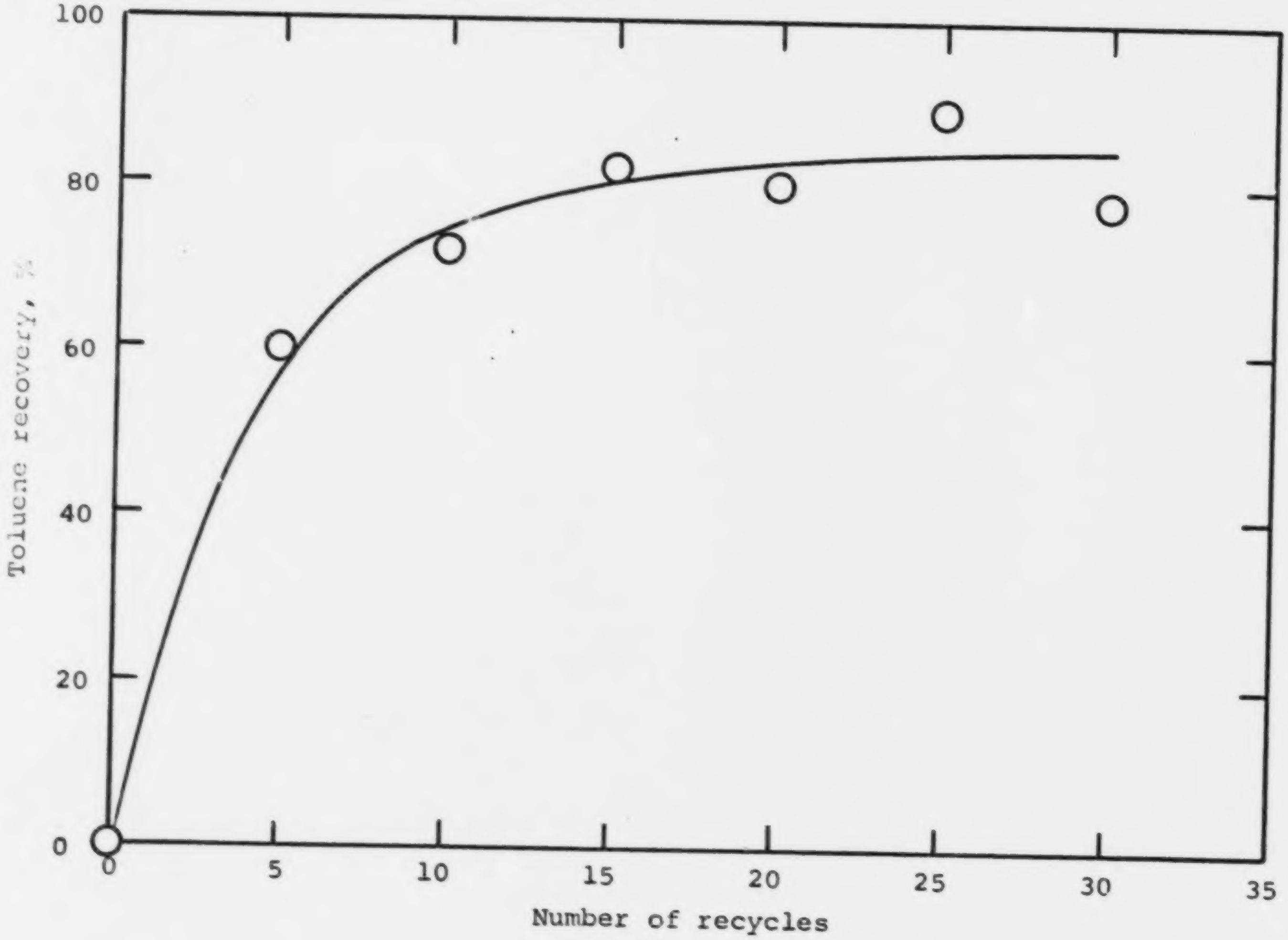


Figure 65 Dependence of Percent Toluene Extracted with Chloroform from Activated Carbon on Number of Soxhlet Extraction Cycles (time/cycle ≈ 12 min.)

that more care would have to be exercised in measuring this parameter. Having maximized the elution process, the other area requiring improvement was in using a better defined starting material and ensuring that the handling and storage did not result in evaporative losses. Since the condensable exhaust from outboard engines was previously shown to consist largely of unburned fuel, a synthetic exhaust condensate was prepared by mixing a known weight of gasoline with water in proportions such that a single phase solution was produced. This synthetic mixture was kept closed from the atmosphere as much as possible before and during actual testing. A gas chromatogram of a $CHCl_3$ extract of the synthetic was then run. The total area of all peaks of the starting material were then compared with that obtained in experimental runs. The results of runs at different flow rates are presented in Figure 66. This curve shows the expected decrease in recovery with flow rate, and a maximum recovery of about 50% was observed.

Effect of Concentration on Recovery --

The dependency of recovery on this parameter was determined by preparing gasoline-water mixtures of compositions ranging from 0.5 ml to 4.0 ml gasoline to 50 gallons water by the method described in the previous section. A flow rate of 600 ml/min through the carbon adsorbers was used in all

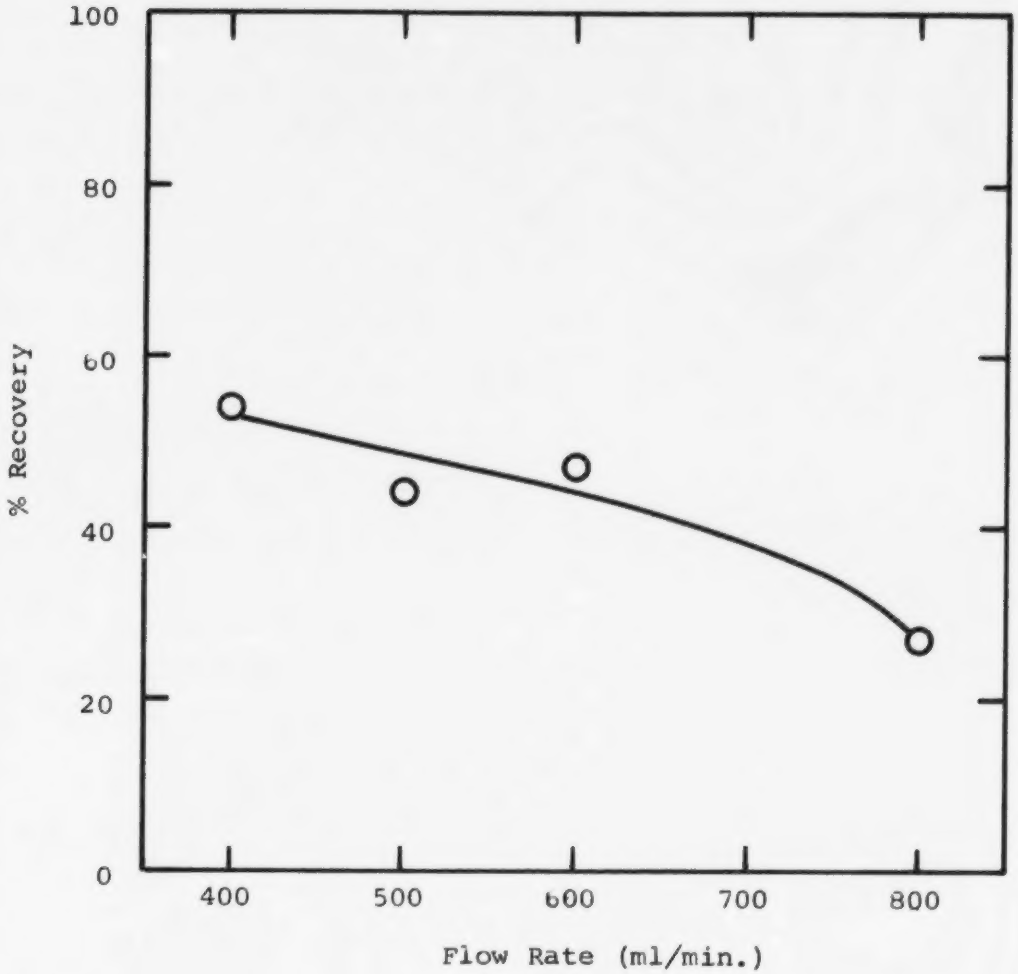


Figure 66 Recovery of Toluene From Activated Carbon Adsorbers with Flow Rate-Wet Extraction

cases. Work-up and analysis was by wet extraction and gas chromatography as previously described. The results, presented in Figure 67, show a sharp decrease in recovery at lower concentrations, which is the region of interest for field work.

Thus this method seems to be unsuitable for concentration and analysis of gasoline-type hydrocarbons. Two alternative techniques suggest themselves, i.e., liquid-liquid extraction into an organic phase and the use of a more suitable solid adsorbent than activated carbon. Both techniques were explored as described below.

CYCLOHEXANE EXTRACTION

If a sample of "OME water" was extracted with spectroquality cyclohexane under carefully controlled conditions and the organic phase examined spectrophotometrically in the ultraviolet frequency regions, a reasonably good correlation between fuel burned and absorbance at 210 nm was obtained. A typical spectrum is shown in Figure 68.

Experimental Conditions

In a 1-gallon jug, a 3.5 l sample of the solution to be analyzed and 50 ml of spectroquality cyclohexane are rapidly stirred for 5 minutes under conditions on minimal exposure to

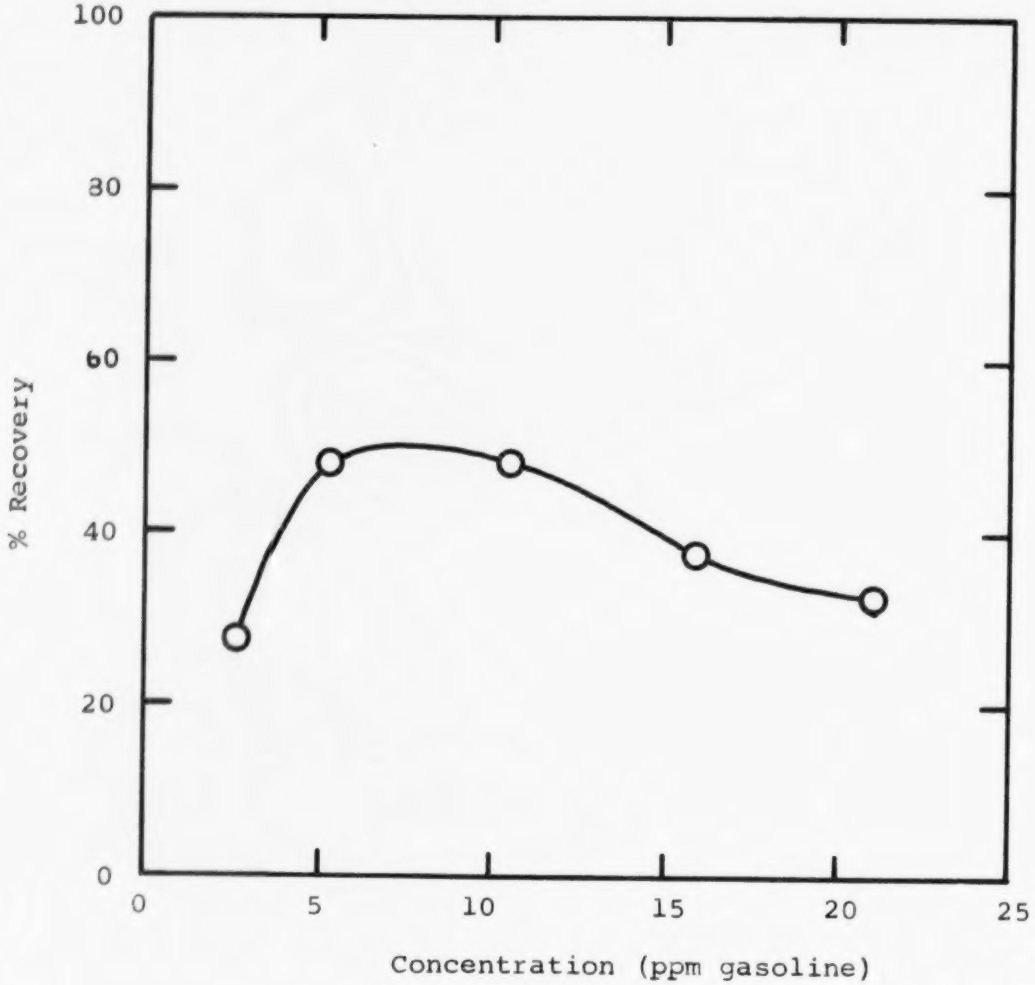


Figure 67 Recovery of Toluene from Activated Carbon Adsorbers vs. Initial Concentration in the Aqueous Phase

Flow Rate Through Adsorbers = 600 ml/min

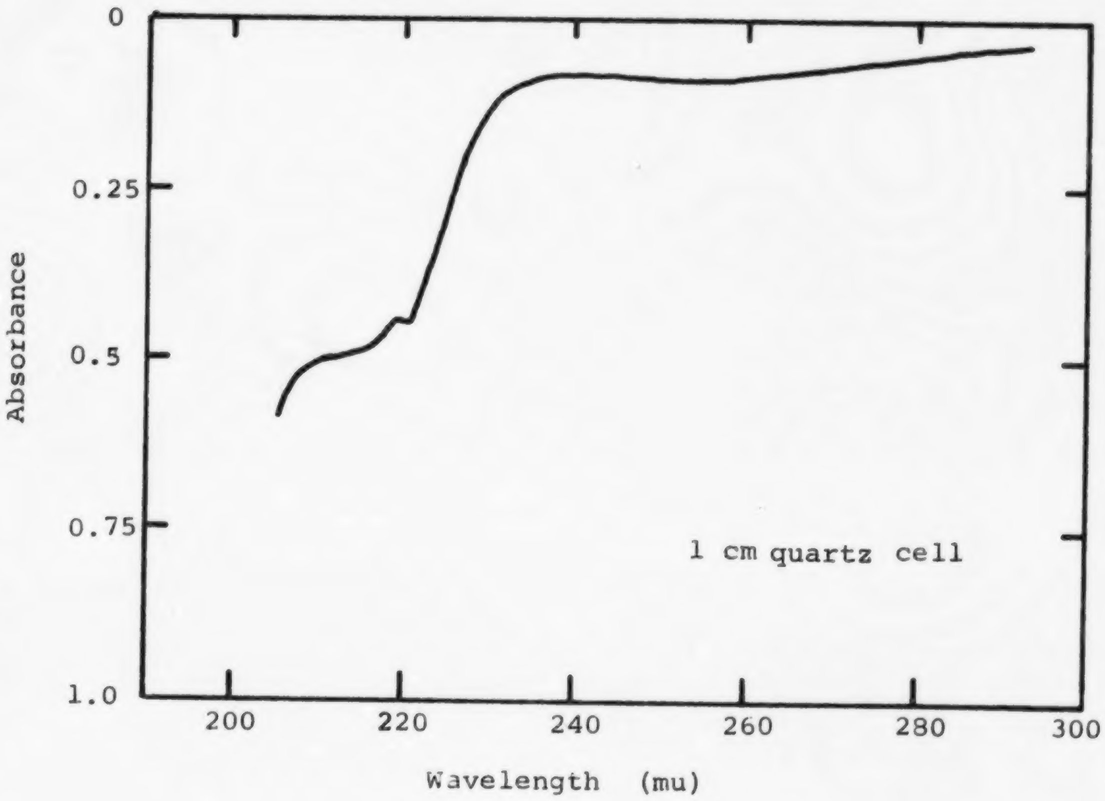


Figure 68 Ultraviolet Spectrum of OME Water Extracted into Cyclohexane

air. After removal of the stirrer, distilled water is added such that the organic phase rises to the neck of the jug. A tight-fitting cap is then placed on the jug and solvent separation allowed to take place for a period of 30 minutes. The apparatus used is shown in Figure 69.

Results and Discussion

Calibration of the absorbance versus concentration relationship was done using toluene, as this is the major mononuclear aromatic component of both the fuel and the condensate. Results are therefore expressed as ppm aromatics as toluene. In field use, however, this method would suffer from a lack of specificity, i.e., it measures extractable aromatics, whether hydrocarbons or not and whether derived from engine usage or not. Furthermore, as time progresses and evaporation takes place, the residual aromatic species in the water column derived from outboard usage are less and less well represented by the condensate and become more enriched in the heavier aromatics. Expressing aromatic concentration as toluene becomes, therefore, less useful. In the absence of any better index, however, this was the method used.

As can be seen from the above, a method was needed which would allow a more definite assignment of hydrocarbons found

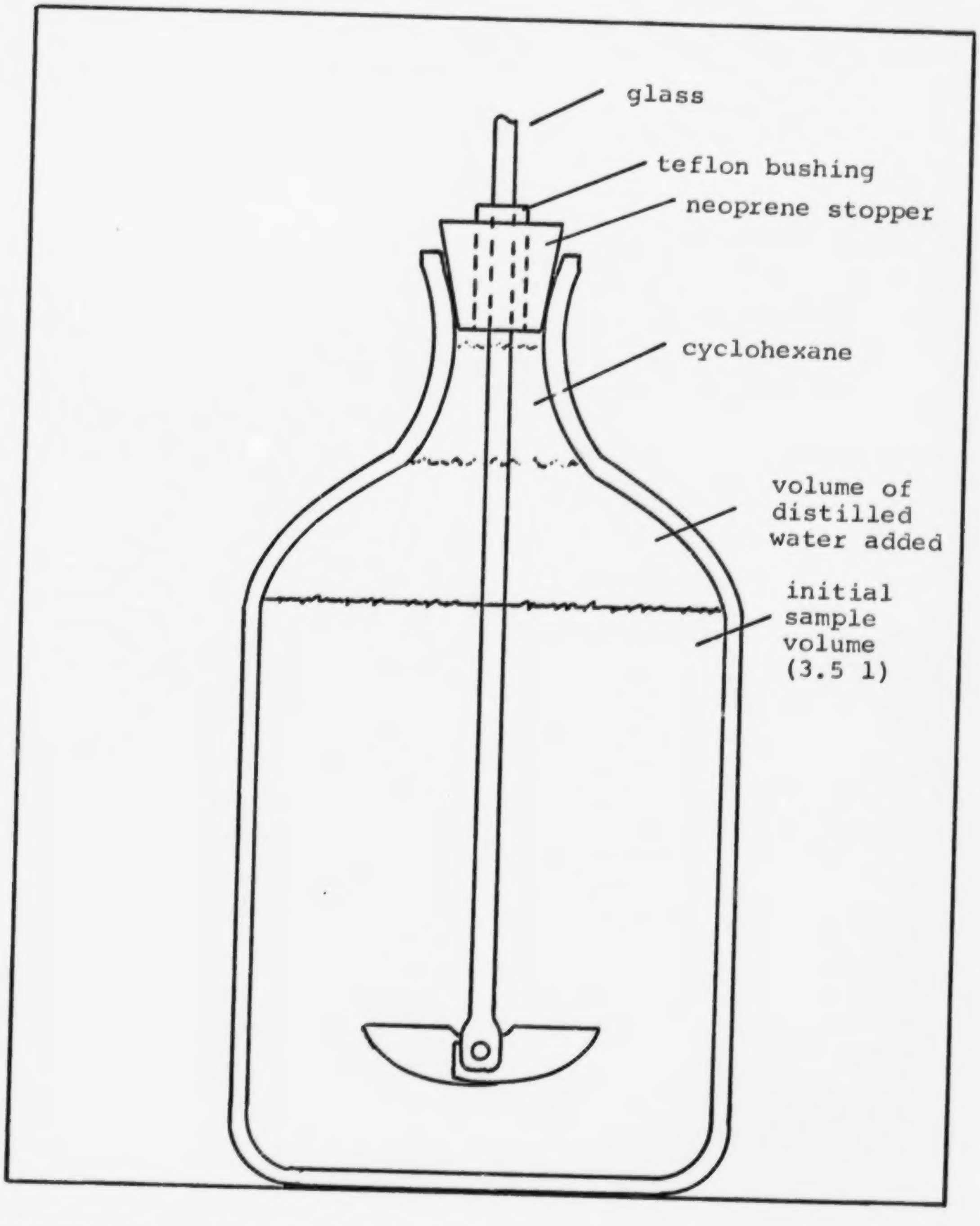

glass
teflon bushing
neoprene stopper
cyclohexane
volume of distilled water added
initial sample volume (3.5 l)

FIGURE 69 Bottle Used for Extraction of UV-active Components from Aqueous Systems Containing Outboard Engine Exhaust Emissions.

in water to outboard engine usage.

MACRORETICULAR RESIN METHOD

A macroreticular resin of the same kind as that used to concentrate "neutral" organic compounds from water (29) was obtained from Rohm and Haas Co.; the resin is named XAD-2 by the manufacturer

Analytical Methods

Profiting from the experience with the carbon adsorption scheme, a flow-through system was set up in which evaporation was minimized and flow rate easily controlled. The apparatus is shown in Figures 70 and 71. Flow rate is adjusted by balancing the vacuum applied to the bottom of the column against the bleed (vent valve). Measurement of flow rate is accomplished using a graduated cylinder as a receiver; it can be emptied without perturbing the system by vacuum aspiration. Evaporation of volatiles is minimized by use of cover on the reservoir which floats on the surface. Recovery was studied as a function of: 1) concentration of aromatics; 2) relative concentration of exhaust components; 3) flow rate; and, 4) amount of eluent.

Preparation of Columns --

A 0.5-cm diameter glass column was packed with dry resin

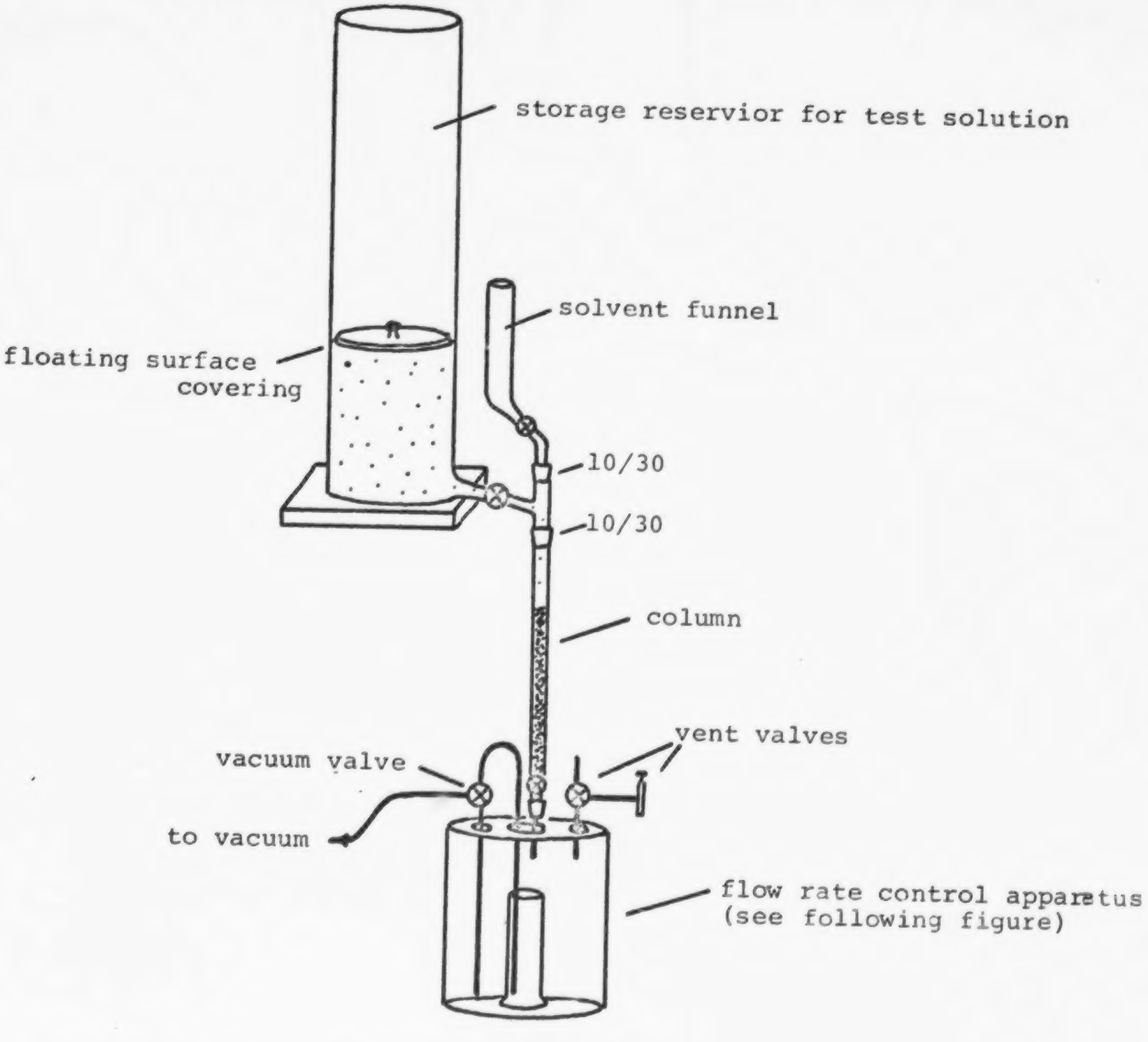

storage reservior for test solution
solvent funnel
floating surface covering
10/30
10/30
column
vent valves
vacuum valve
to vacuum
flow rate control apparatus (see following figure)

Figure 70 Macroreticular Resin Apparatus: Reservoir, Column, and Flow Rate Control.

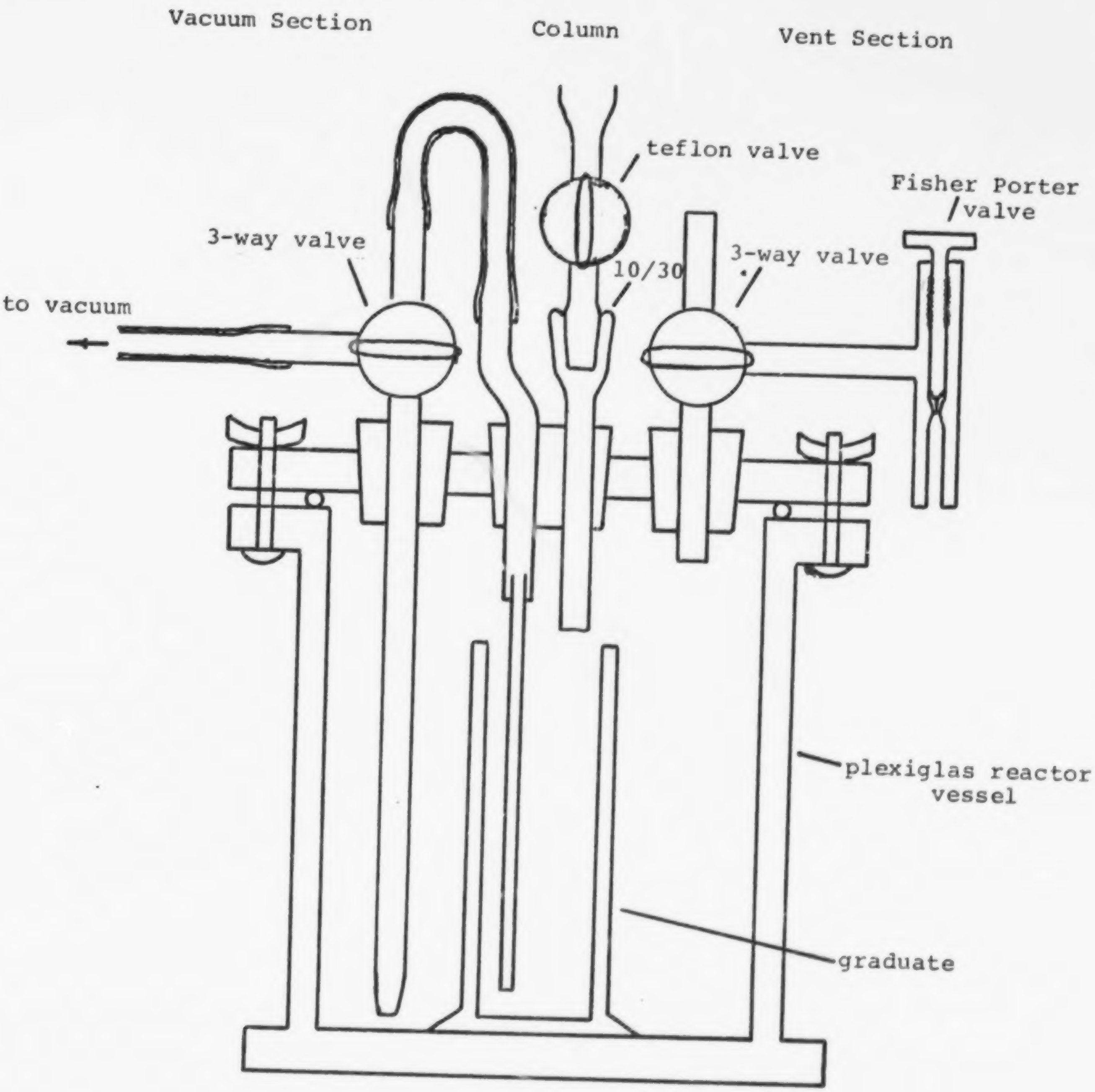

Vacuum Section
Column
Vent Section
teflon valve
Fisher Porter
valve
3-way valve
10/30
3-way valve
to vacuum
plexiglas reactor vessel
graduate

Figure 71 Macroreticular Resin Apparatus: Flow Rate Control.

Glass wool plugs were placed at the top and bottom of the resing. The column was then washed with 20-25 ml of $CHCl_3$ elution solvent, then 100 ml of ethyl alcohol and finally with several liters of distilled water until the ultraviolet absorbance of the wash was zero. The organic-containing solution was then passed through the resin column, the column eluted and the eluent examined by gas chromatography using a 3% PMPE on 80/100 chromosorb W 1/8 in S.S. column. Helium was used as carrier gas at 30 ml/min; isothermal conditions at 100 °C were used.

Results and Discussion

Dependence of recovery on concentration

Conditions

Column: 3 g XAD-2

Test solution: 4 liters of solution for each of several samples containing from 50 to 295 ppb of toluene

Flow rate: 30 ml/min

Eluent: 10 ml $CHCl_3$

A plot of the % recovery versus concentration is shown in Figure 72. The results show a fairly high recovery not strongly dependent on initial concentration.

Dependence of recovery on relative composition of exhaust components

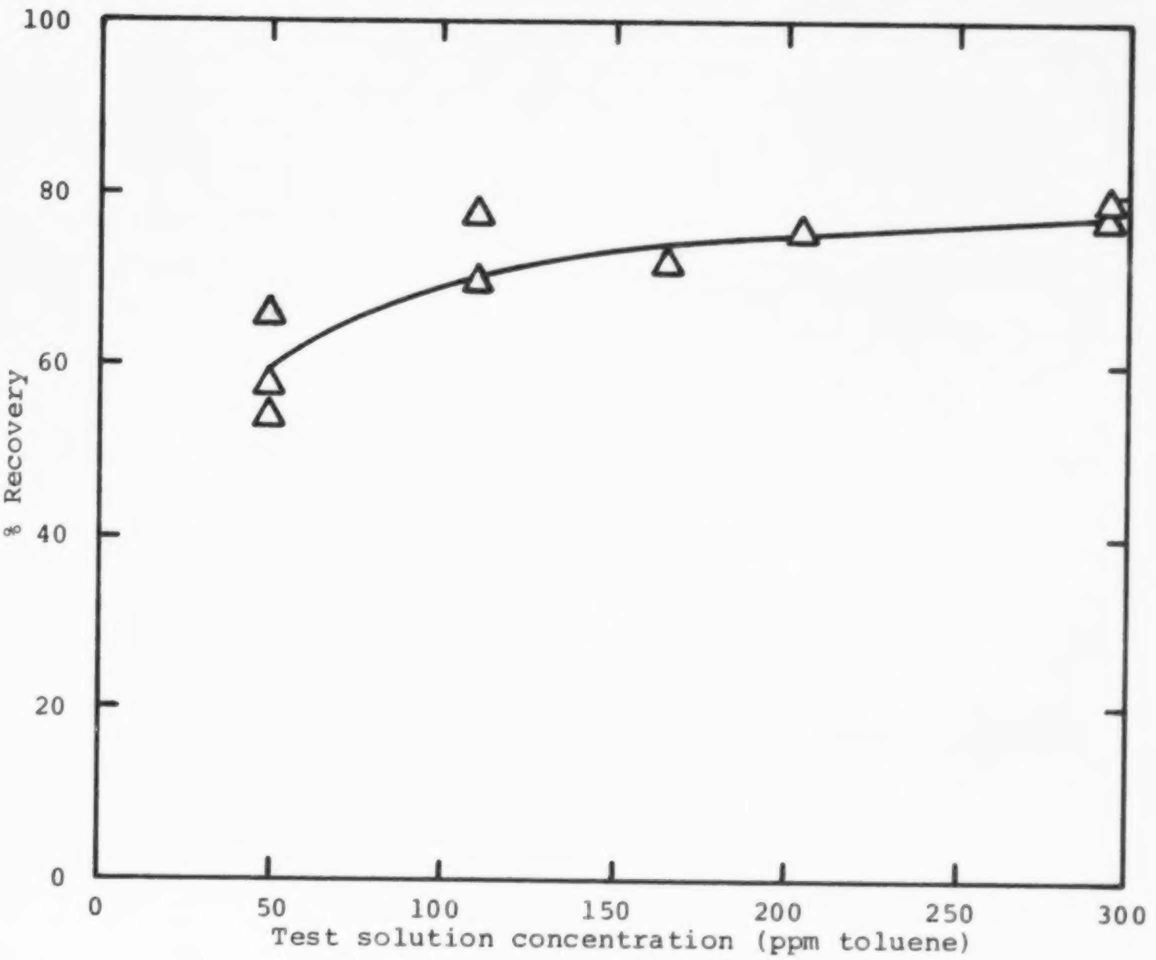


Figure 72 Recovery of Toluene from Aqueous Solution by Adsorption on XAD-2 Resin and Desorption with $CHCl_3$

Conditions

Column: 3 g XAD-2 resin

Test solution: 4 l of a mixture of 165 ppb toluene, 60 ppb m-xylene and 21 ppb 1,2,4 trimethylbenzene

Flow rate: 30 ml/min

Eluent: 10 ml $CHCl_3$

Percent recoveries for 2 runs were:

Run #	toluene	xylene	TMB
1	70%	67%	80%
2	85%	61%	78%
average	78%	64%	79%

Recoveries were quite good for all components.

Dependence of recovery on flow rate

Conditions

Column: 3 g XAD-2

Test solution: 4 l of 100 ppb toluene

Flow rate: varied between 15 and 40 ml/min

Eluent: 10 ml $CHCl_3$

Figure 73 shows the results. Except at low flow rates, recovery is relatively insensitive to this parameter, and at the flow rate used in these tests, 30 ml/min, small deviations in flow rate have practically no effect at all on recovery. While higher recovery could be obtained using a flow rate through the adsorber of 15 ml/min, for practical

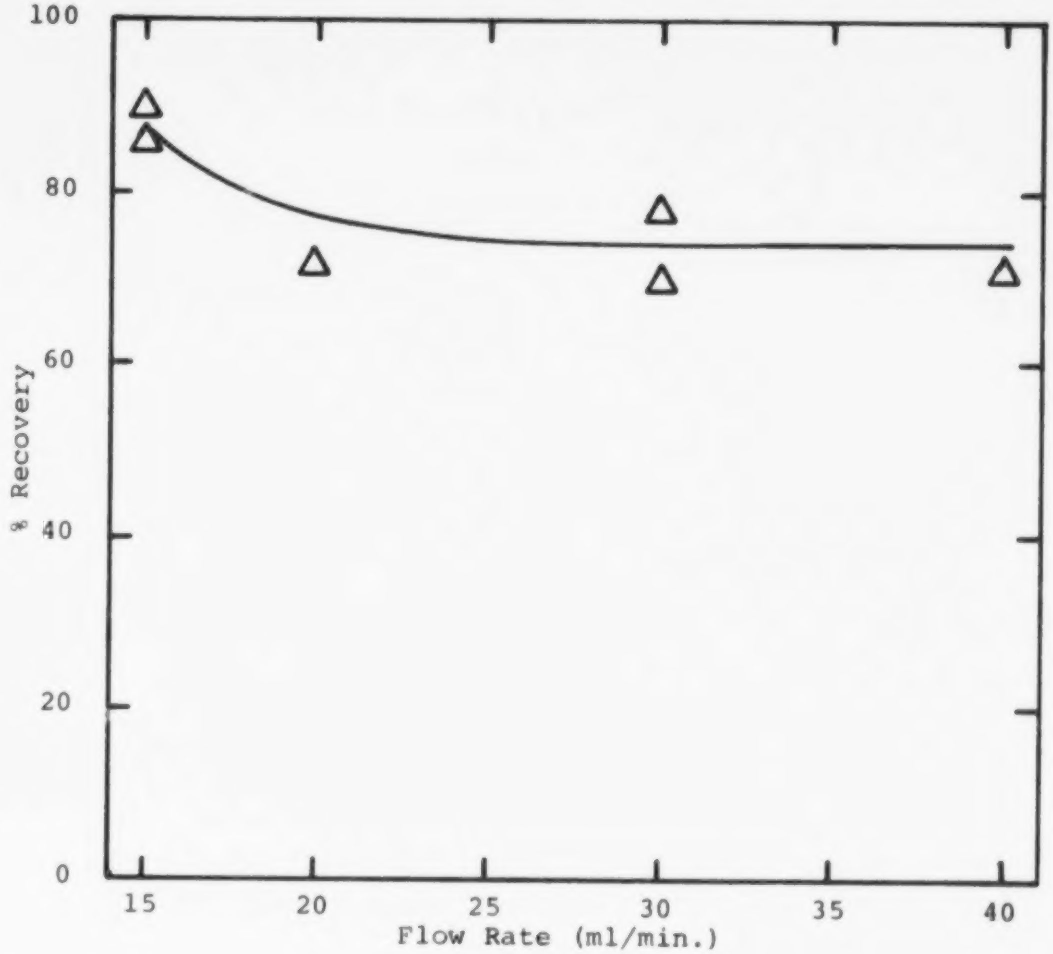


Figure 73 Recovery of Toluene from Aqueous Solution by Adsorption on XAD-2 Resin as a Function of Flow Rate

reasons of the time necessary for processing large volumes of water, the higher flow rate was adopted.

Dependence of recovery on eluent volume

If a second 30 ml portion of $CHCl_3$ was passed through the adsorber column following the runs described in part 3, no detectable amount of aromatics could be found in the second eluent. Therefore 30 ml is sufficient to elute all the adsorbed material.

In sum, the XAD-2 resin was shown to be a useful method of recovering exhaust products, more particularly the mononuclear aromatic products from aqueous solution. A comparison between a direct ultraviolet absorption measurement on "OME water" with the cyclohexane extraction method and the resin method is shown in Figure 74. The data shows that while the two U.V. methods gave essentially the same results, the resin technique gave consistently lower results. The major reason for this is probably that, in fact, both the U.V. methods measure total aromatics while the resin technique measures mononuclear aromatics only. In the case of "OME water," the more gas consumption the longer engine running time and, at least in this fixed volume situation, the more evaporation aided by the sparging effect of propeller action. Thus one would expect a continuously widening difference between total aromatics and the volatile mononuclear aromatics, which is

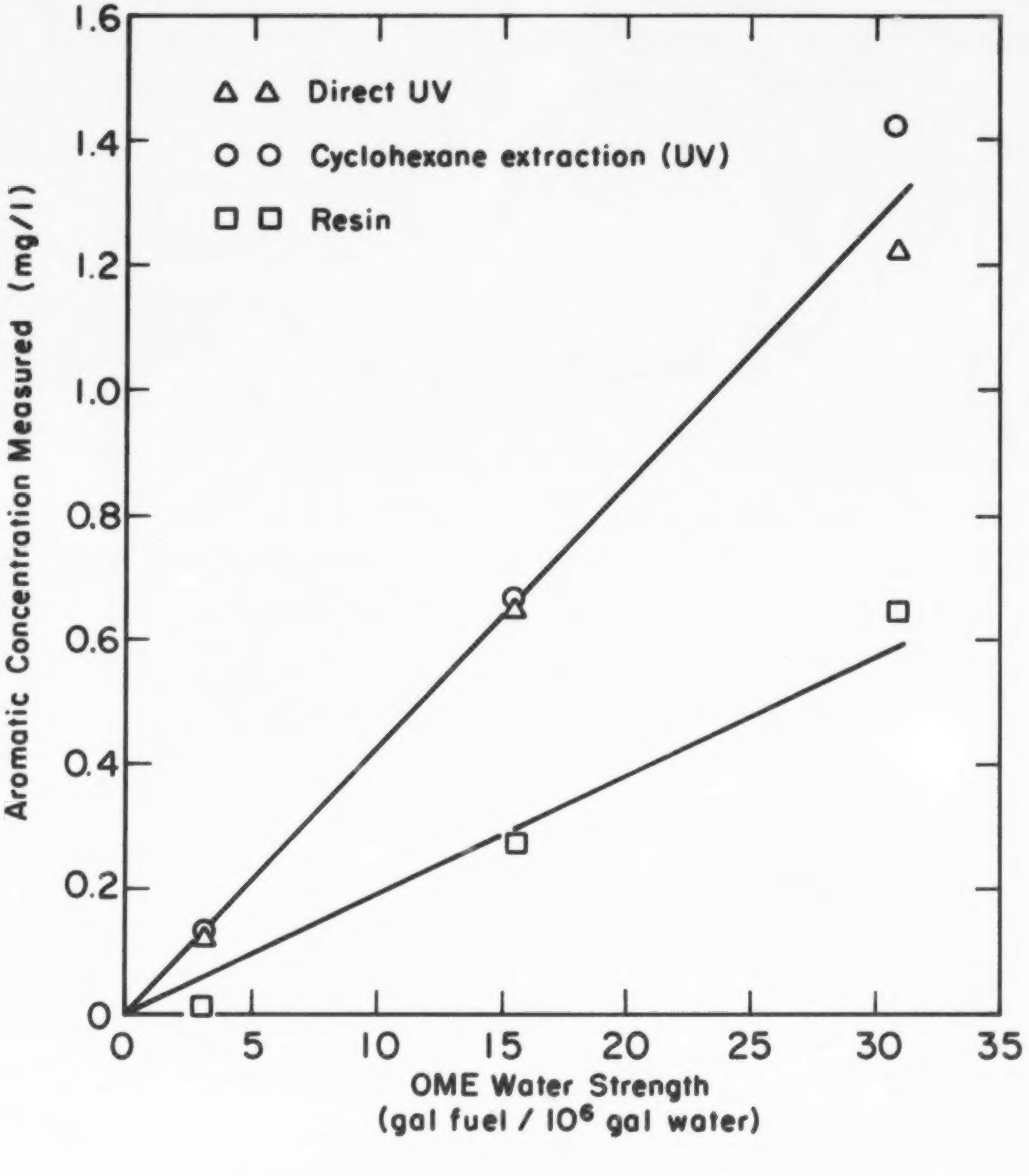


Figure 74 Aromatic Concentration in OME Water, Analyzed by three Methods

what is observed.

Analyses by these methods is reported in the ENCOTEC report. However, it is instructive to examine the results obtained in examining their test ponds, which are presented below (extraction method)

	Oct. 5	Oct. 12	Oct. 20
Pond #1 (non-leaded)	0.27	0.24	0.08
Pond #2 (control)	0.09	--	0.07
Pond #3 (leaded)	0.19	0.20	0.12
Pond #4 (control)	0.09	0.11	0.09

As can be seen, stressed ponds were found to have higher levels of aromatics than did the controls. However, they differ only by a factor of three at a maximum. The levels of aromatics found in these highly stressed ponds was therefore always of the same order of magnitude as the natural background level. The increases in aromatic concentration are probably attributable to outboard engine usage, however, such small differences tend to be swamped out by periodic fluctuations of the natural background levels of aromatics. During the monitoring of the ponds in Saline a very sudden large increase in aromatic content was noted. When the resin technique was applied to the pond water no detectable level of mononuclear aromatics was observed; therefore, it was quite unlikely that this increase was related to outboard engine usage. The two analytical techniques can in this way be viewed as complementary.

SECTION VIII

FISH TOXICITY STUDIES

To test whether outboard engine exhaust components could be implicated in fish mortality, it was necessary to determine the acute toxicity of the various pure hydrocarbon species identified as present in exhaust emissions and most likely to be acutely toxic, and of the total outboard engine exhaust condensate itself. Some initial difficulties were encountered in developing a stable fish population for testing. Fat head minnows (Pimephales promelas) proved to be unsuitable for this reason and the study was therefore pursued using the more hardy goldfish (Carassius auratus). Because of the fairly rapid evaporation of toxic components (described in a previous section), conventional static fish toxicity studies were deemed unsuitable, and a dynamic testing system was devised whereby fresh solutions of the toxic components studied were continuously fed to test aquaria.

EXPERIMENTAL METHODS

Figure 75 depicts the experimental apparatus schematically.

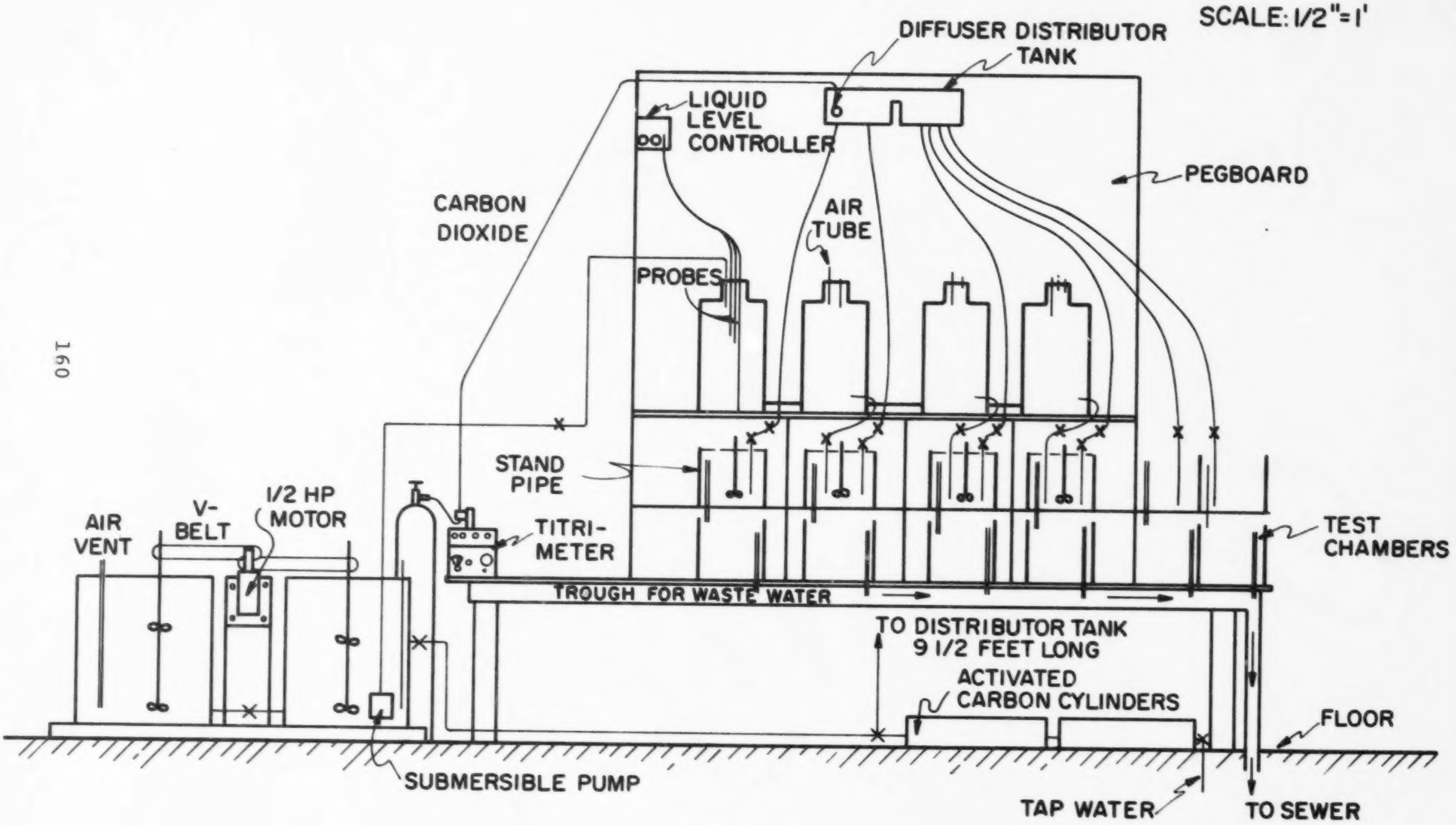

SCALE: 1/2"=1'
DIFFUSER DISTRIBUTOR
TANK
LIQUID
LEVEL
CONTROLLER
PEGBOARD
CARBON
DIOXIDE
AIR
TUBE
PROBES
STAND
PIPE
TITRI-
METER
AIR
VENT
V-
BELT
1/2 HP
MOTOR
TEST
CHAMBERS
TROUGH FOR WASTE WATER
TO DISTRIBUTOR TANK
9 1/2 FEET LONG
ACTIVATED
CARBON CYLINDERS
FLOOR
SUBMERSIBLE PUMP
TAP WATER
TO SEWER

Figure 75 Schematic Diagram of the Experimental Apparatus Used for Fish Toxicity Studies

As shown in Figure 75, Ann Arbor tap water flows through two carbon filters 61 cm X 15 cm each (2 feet X 6 inches) which effectively dechlorinates the water by reducing the active compounds of chlorine to chloride. The dechlorinated tap water moves through 1.77 cm polyvinyl chloride (PVC) pipe (Schedule 80) to two 208-liter (55-gallon) drums. These drums have a dual capability of holding either a stock solution of OME water or a stock solution of individual toxic hydrocarbons found in OME water. The stock solution of OME water is made by running either non-leaded gasoline (Indolene Clear) or leaded gasoline (Indolene 30, containing 0.79 g per liter or 3 g per gallon of tetraethyl lead) through two 2 hp Johnson outboard motors into a 208-liter (55-gallon) drum. The amount of fuel run through the engines is monitored using 250 ml dispensing burets with stopcocks. The amount of water in the 208-liter (55-gallon) drums has been calibrated and is controlled by overflow pipes. One drum holds 200 liters (52.84 gallons) of water, while the other holds 207 liters (54.69 gallons) of water. Therefore, the concentration of stock solution of the OME water is easily calculated. Exhaust fumes from the outboard motors are vented through exhaust hoods. The stock solution of pure compounds found in OME water is made by pouring a known quantity down the air vent into each 208-liter (55-gallon) drum. A homogeneous solution is made by vigorously mixing each drum simultaneously with a 1/2 hp motor (1725 rpm) driving two stirrers via V-belts. Each drum is covered with a 3.18-mm (1/8-inch) piece of aluminum sealed with rubber weather stripping, and fastened down with four 1.77-cm (1/2-inch) eye bolts. As a consequence, there is very little evaporation of the stock solution from the drums. The drums are interconnecting allowing the identical stock solution from one drum to flow to the other. A submersible pump is located in one drum with a long glass (10-mm) tube coming off the pump, going through a neoprene rubber stopper in the aluminum cover to a wide-mouth, 19-liter (5-gallon) glass jug. A liquid level controller (Dyna Sense Electronic, Model 7186) via glass probes automatically controls the levels of the stock solution entering the first jug from the drum. Jugs 2, 3, and 4 are filled from connections going from jugs 1, 2, and 3. Gravity flow through glass tubine and 4-mm stopcock glass valves controls the flow rate of the stock solution from the jugs to the constantly stirred reactor chambers. Since water from the jugs comes via gravity flow from the bottom of the jugs, pressure changes in the jugs due to water level changes in the jugs were of great concern. This problem was resolved by maintaining a nearly constant level of liquid in the jugs, putting the upper and lower probes from the liquid level controller close together and using the jug with these probes in it for a storage vessel only. In this way there was just a short drop in head pressure compared to the overall head. Therefore, according to Bernoulli's Equation, pressure changes and the resultant flow rate changes from just a small change in overall height of the liquid were negligible. Using Bernoulli's Equation and Torricelli's Theory, it was determined that the variations in head pressure introduced approximately a 2% error, which is negligible and most difficult to measure with a stop watch and glass cylinder.

The rest of the continuous-flow bioassay system consists of sending tap water, treated with carbon dioxide to lower the pH, to the constantly stirred reactors from a constant head distributor tank. The tap water is then sent through glass tubing and 4-mm stopcock glass valves which control the flow rate. Flow rates are fast enough to renew the volume in the test chambers every 1 1/2 hours. Fish receive doses of this homogeneous mixture from a standpipe in the reaction chamber. All reaction chambers are covered with 3.18-mm (1/8-inch) aluminum sheets. The glass tubes going through this sheet are inserted through neoprene stoppers, and the rod from the stirrer blade goes through a teflon bushing to the 1550-rpm mixer. A rubber seal between the top edge of the reaction chamber and the 3.18-mm (1/8-inch) aluminum sheet with 11.34 kg (25 lb) of weight on it makes a tight seal. Water from the test chambers flows through a standpipe to a collecting trough which empties into the sewer, thus completing the continuous-flow system. Artificial lighting is provided by a row of 40-watt fluorescent lamps 61 cm (24 inches) above the water surface. These lamps are controlled on a 24-hour cycle by a timing device which is adjusted to approximate the natural photoperiod. Natural seasonal variations in ambient temperature are used for the tests because it was too costly to heat or cool this water at such a high flow rate.

The LC-50 was used as a statistical measure of acute toxicity in order to specify the lethal concentration of leaded OME water, non-leaded OME water, toluene, mixed xylene, and 1,3,5 trimethylbenzene. The specific compounds were used in this experiment because these are three of the aromatic components that have been found in appreciable amounts in OME water. Deaths of goldfish in a range of concentrations were recorded from 24 to 96 hours so that dose-response curves could be determined by a computer program.

Continuous-flow bioassays were used in all 96-hour tests. The design of the apparatus has been described in the text and a schematic presented in Figure 75. The basic procedure for the leaded and non-leaded OME emission experiments consisted of making a stock solution of the OME emissions by running a known concentration of fuel at the recommended 50:1 fuel:oil ratio through a Johnson 2 hp engine at full throttle. After the stock solution was prepared, the engine was removed from the 208-liter (55-gallon) tank and the solution tank was immediately covered with a 3.18-mm (1/8 inch) thick aluminum cover to prevent evaporation of exhaust emission from the water. Care was taken to avoid phase separation in the receiving waters by restricting fuel consumption to the region where the ultraviolet absorbance of the aqueous phase was linear with fuel used. Furthermore, the stock solution was renewed every 12-16 hours. The dispensing of the stock solution has been explained on page 161. As mentioned, dechlorinated Ann Arbor tap water with an adjusted pH was used in all experiments (See Table 13 for Ann Arbor Tap Water Analysis). Adjustment of pH was accomplished by bubbling gaseous CO_2 into the tap water using a Fisher automatic titrimeter (Model 36). The pH varied in the test chambers from 6.8 to 7.3 throughout the 96 hours of testing for each experiment. Water temperature varied from 17-19° C throughout the testing period. Dissolved oxygen (D.O.) was checked initially using the Azide Modification of the Iodometric Method (Modified Winkler) as described in Standard Methods, 1965. However, the D.O. was always 7

Table 13 Ann Arbor Tap Water Analysis*

Methyl orange alkalinity	34 ppm as $CaCO_3$
Phenolphthalein alkalinity	37 ppm as $CaCO_3$
Hydroxide alkalinity	3 ppm as $CaCO_3$
Bicarbonate alkalinity	0 ppm as $CaCO_3$
Total hardness	80 ppm as $CaCO_3$
Non-carbonate hardness	46 ppm as $CaCO_3$
pH	10.0
Chlorine	0.5 - 0.7 ppm
Calcium	21.6 ppm
Magnesium	5.3 ppm
Chromium	<0.002 ppm
SiO_2	8 ppm

* Analysis determined by a research team from the Department of Civil Engineering, The University of Michigan, under the direction of Dr. Walter J. Weber, Jr.

ppm or higher because of a rapid turnover of water. Flow rates were frequently checked, and UV analysis (Beckman DU) was used to monitor the system at all times. The outboard motor exhaust water was monitored as parts per million of toluene. The exact same procedure was used for the toluene, mixed xylene and 1,3,5 trimethylbenzene experiments, except that the stock solutions were made in parts per million by mixing the aromatic compounds and water vigorously with two large mechanical stirrers for 10 minutes. Finally, varying concentrations of OME water or pure compounds found in OME water were dispensed continuously to open aquariums housing six goldfish each, measureing between 12.70-20.32 cm (5-8 inches) in length and weighing from 20-80 grams. The fish varied in age from 1 to 1 1/2 years old.

RESULTS AND DISCUSSION

The determination of 24-, 48-, 72-, and 96-hour LC-50's for leaded OME water, non-leaded OME water, toluene, mixed xylene, and 1,3,5, trimethylbenzene revealed that goldfish can withstand relatively high concentrations of these compounds. Other researchers have reported higher concentrations than found in this study because they used static tests instead of continuous flow tests for their experiments and lost most of their original concentrations by evaporation during the first 24 hours. For instance, Pickering and Henderson (30) reported 96-hour LC-50 values for toluene and xylene of 59 and 35 ppm, respectively, while this study reported 23 and 17 ppm for these same compounds (Table14). Furthermore, the results of Wallen et al. (31) appear as if they used super-saturated systems to get their dilutions because they reported a 24-hour LC-50 for toluene in mosquitofish (*Gambusia affinis*) of approximately 1000 ppm. They said also that all fish were normal at 560 ppm and below. Although Wallen et al. (31) used a different species of fish than those used by Pickering and Henderson (30) and those used in this study, there should not be a difference of this magnitude. Also, McKee (32) reports that toluene has a solubility of only 470 ppm in water at 16 °C. As a consequence, it is concluded that all LC-50 data with highly volatile and evaporative compounds, such as aromatic hydrocarbons should be reexamined using continuous flow bioassays. The continuous flow bioassay system for aromatic compounds should have the capability of fast renewal of the compound being tested, good mixing of these compounds to achieve homogeneous conditions, and should be enclosed as much as possible to prevent evaporation of these compounds. Furthermore, it is most important to stay within the solubility limits of the compound being tested or the results will be completely misleading.

Another important difference between the results of this study and those of other researchers is that the 96-hour LC-50's are lower than the 24-hour LC-50's for all the compounds tested. In contrast, Pickering and Henderson (30) did not find any lower values for their 96-hour tests as compared to their 24-hour tests for toluene and xylene with goldfish. The reason for this again is that they used static tests for their experiments and lost most of their original concentrations by evaporation probably before the first 6 hours of the LC-50 test. English et al. (5) have shown that there is a decrease in acute toxicity of OME water upon aging.

Tables 14 and 15 show the results for the two major aromatic constituents of the condensate and for exhaust condensate derived from engines using leaded and non-leaded gasoline. Figure 76 gives the conversion of the fuel to receiving water ratio to aromatic content as ppm of toluene. As can be seen from this comparison, the exhaust products are somewhat more toxic than the pure aromatic species, but of the same order of magnitude. These findings along with the results for aromatic concentration at steady state in the test ponds (ENCOTEC report) show that even under their

TABLE 14

Median Tolerance Limits for Goldfish Exposed to Aromatic Hydrocarbons

	LC-50 Values (ppm)			
Compound	24 hr.	48 hr.	72 hr.	96 hr.
Toluene	41.6	27.6	25.3	22.8
Xylene	30.6	25.1	20.7	16.9

TABLE 15

Median Tolerance Limits for Goldfish Exposed to Outboard Engine Exhaust Water

	LC-50* for Exposure Time			
Fuel	24 hr.	48 hr.	72 hr.	96 hr.
Non-leaded	212 (1/4720)	194 (1/5160)	185 (1/5410)	168 (1/5960)
Leaded	226 (1/4420)	204 (1/4920)	192 (1/5220)	171 (1/5860)

*Values given in terms of gallons of fuel burned per million gallons of water (ppm by volume).

Values in parentheses given as the volume ratio of fuel to dilution water.

See Figure 76 for Toluene Number associated with OME water strength.

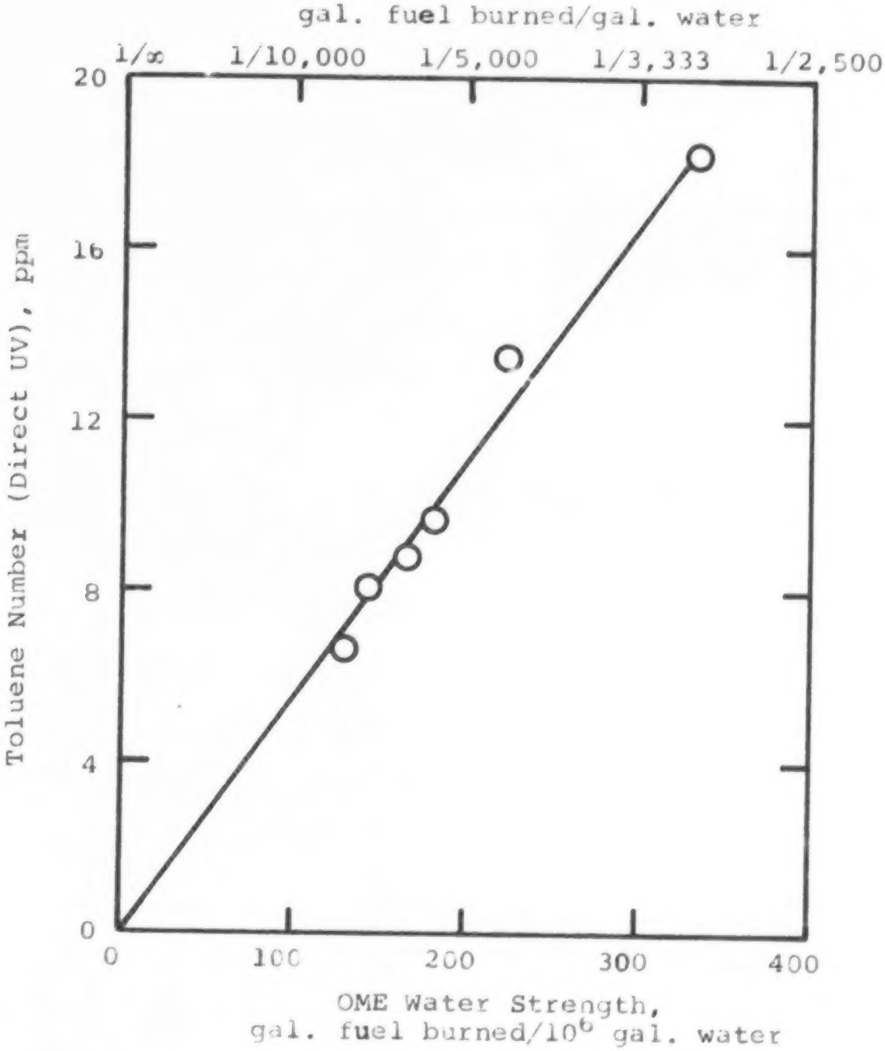


Figure 76 Relationship of OME Water Strength to Aromatic Concentration as P.P.M. Toluene

conditions of extreme levels of stress, steady-state levels of aromatics were 2 to 3 orders of magnitude less than the LC-50 values for the test fish. Complete data are to be found in Appendix B.

SECTION IX

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SECTION X

APPENDIX A

Hydrocarbon Analyzer Sensitivity

NDIR: The NDIR analyzer is sensitized to a single component, n-hexane (C_6H_{14}) which is supposedly representative of the average unburned hydrocarbon molecule in the engine exhaust. But, since the exhaust hydrocarbons actually consist of over 200 different hydrocarbon species one must look at the response of the n-hexane detector to the various species before an accurate prediction of total exhaust hydrocarbon content can be made. Unfortunately, only the infrared absorption spectrum of the paraffinic compounds, except methane, compares favorably with n-hexane. Thus, the analyzer will respond to only the paraffinic carbon atoms on close to a one-to-one basis. The response of the NDIR to the exhaust olefins, diolefins, and aromatics is quite low. The average relative response of the NDIR to a few of the most important exhaust hydrocarbons is shown in Table 1. Because several sample cell lengths are commonly used in the NDIR analyzer (a greater length cell is used to increase the sensitivity) the relative response is stated for three typical lengths. In our two-stroke engine work we have used the least sensitive, 2-1/2 in. cell.

No relative response is stated for the oxygenated hydrocarbons (aldehydes, ketones, etc.) because these components

TABLE 1

HYDROCARBON RELATIVE RESPONSE OF THE NONDISPERSIVE INFRARED ANALYZER (15)

Compounds	Average Relative Responses on Carbon Basis		
	2-1/2 in. Sample Cell	5-1/4 in. Sample Cell	13-1/2 in. Sample Cell
Paraffins			
Methane	29	30	30
Ethane	100	100	100
Propane	102	103	103
n-Butane	101	101	101
i-Butane	105	106	106
i-Pentane	99	99	99
n-Pentane	105	104	104
n-Hexane	100	100	100
n-Heptane	97	97	97
Olefins			
Ethylene	9	9	9
Propylene	30	31	31
1-Butene	---	53	---
1-Pentene	---	57	---
1-Hexene	---	61	---
Acetylenes			
Acetylene	1	1	1
Methylacetylene	16	16	16
Ethylacetylene	33	32	32
Aromatics			
Benzene	2	2	2
Toluene	12	13	13

are removed from the sample in the condensate trap before entering the analyzer. This is likewise true in the FID system.

FID: The FID analyzer responds well to a broad range of hydrocarbons. In fact, with only a few exceptions, it responds almost linearly to the number of organic carbon atoms in the exhaust hydrocarbon molecules. The acetylenes, however, are an exception to the rule. Table 2 shows the relative response of the FID to the most important exhaust hydrocarbons for two hydrogen-diluent (H/D) ratios in the analyzer. The H/D ratio is the ratio of the FID fuel flow rate (by volume) to the sample flow rate. In our studies we have used an H/D ratio of approximately .6.

Subtractive Column Analyzer

The subtractive column analyzer is shown schematically in Figure 8 of the text. Basically the sample is directed alternately to the packed columns or scrubbers. An automatic cycling timer is incorporated to regulate and control the time of flow in the scrubbers. The timer operates solenoid valves that divert the sample flow through a single scrubbing system, while the scrubbers not in use are maintained in a "backflush" condition to purge any incompletely absorbed materials.

The University of Michigan subtractive column unit was checked against a gas chromatograph, Beckman GC-4, at the

TABLE 2

RELATIVE HYDROCARBON RESPONSE OF THE BECKMAN FLAME-IONIZATION ANALYZER (15)

Compounds	H/D* 0.6	H/D* 4.0
Paraffins		
Methane	119	105
Ethane	106	102
Propane	104	103
n-Butane	104	103
i-Pentane	102	101
n-Pentane	103	102
n-Hexane	102	100
n-Heptane	100	100
Olefins		
Ethylene	105	104
Propylene	105	104
Acetylenes		
Acetylene	156	97
Methylacetylene	120	97
Ethylacetylene	125	98
Aromatics		
Benzene	103	109
Toluene	103	109

* H/D = Hydrogen to Diluent Ratio

Ford Motor Company Engineering Staff. The tests were run using exhaust from an idling 2000 cc Pinto engine. Three series of tests were run.

In the first test, exhaust was passed through the olefin + aromatic subtractor columns and then to the G.C. The following results were obtained (Results as ppm carbon = ppmc):

Paraffins	Olefins & Acetylenes	Aromatics	Total
1087	19	44	1150

The analyzer would report 1150 ppmc as paraffins rather than the correct 1087. Thus the error in reporting paraffins was +63/1087 or +5.8%. Our analyzer overestimated the paraffin content of the exhaust by 5.8%.

In the second test additional exhaust gas was passed through the olefin subtractor only. The results were:

Paraffins	Olefins & Acetylenes	Aromatics	Total
1344	27	1130	2501

The analyzer would report 2501 ppmc as paraffins and aromatics rather than the correct 2474. Thus the error in reporting paraffins plus aromatics was +27/2474 or +1.1%. The error in reporting aromatics alone must be estimated since the emission base line shifted between tests. If it is assumed that the subtractive column would report paraffins 5.8% too high, then an estimated value would be: 1344 x 1.058 = 1420 ppmc. By differencing, we find 2501 - 1420 = 1081 to be the aromatic content that would be reported by the subtractive column. The error is 1130 - 1081 or 49 ppmc. Thus the subtractive column underestimated aromatics by 49 ppmc or -49/1130 = -4.3%

In the final test, exhaust was passed directly into the G.C. The results were:

Paraffins	Olefins & Acetylenes	Aromatics	Total
1364	1905	1453	4722

In the above test paraffins plus aromatics were 2817 ppmc. From Test 2, this may be assumed to be 1.1% lower than the subtractive column would yield. The subtractive column value would be 2817 x 1.011 = 2848 ppmc. The subtractive column prediction of olefins plus acetylenes would then be 4722 - 2848 = 1874. This is too low by 1905 - 1874 = 31 ppmc or -31/1905 = -1.6%

Based on these G.C. results one can conclude that the subtractive column class results differed from G.C. class results as shown below:

Class	Percent Error
Acetylenes + olefins	-1.6
Aromatics	-4.3
Paraffins	+5.8

Since acetylenes were about 7.5% of the total in these tests, interpreting the subtractive column results to be olefins rather than olefins plus acetylenes would overestimate olefin content by 5.8%.

Considering the nonparaffin constituents which broke through in Test 1, 14 were olefins and 6 aromatics. Of the 14 olefins, 7 were either 2 or 3 ppmc, the rest were less. Of the 6 aromatics, the ppmc contributions were:

Constituent	ppmc after subtraction
Benzene	3
Toluene	17
Ethyl benzene	5
Xylenes	6
Mono substituted ethyl benzenes	8
Di substituted ethyl benzene	5
Total	44

Only 1 or 2% of the smaller aromatics broke through but virtually all of the large aromatics did. This result is different from that of Sigsby(17). In his tests virtually no larger aromatics broke through but a large percentage (>80%)

of benzene did. Fortunately the concentration of the larger aromatics is small.

In conclusion, within the limitations of tests, the accuracy of the subtractive columns was better than 6% in reporting the hydrocarbon classes. The major drawback is that acetylene is reported as an olefin.

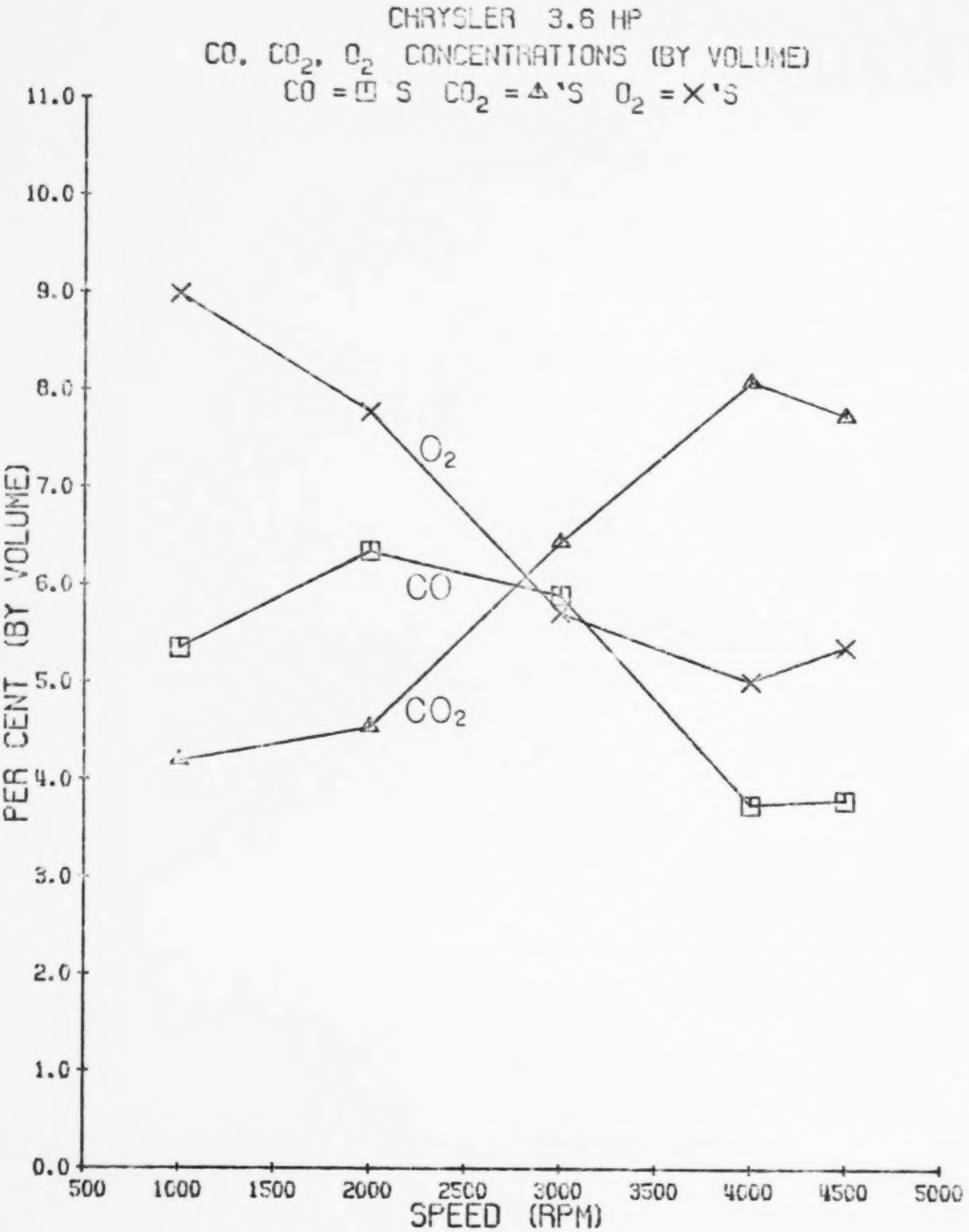

Figure 1 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 3.6 hp Chrysler

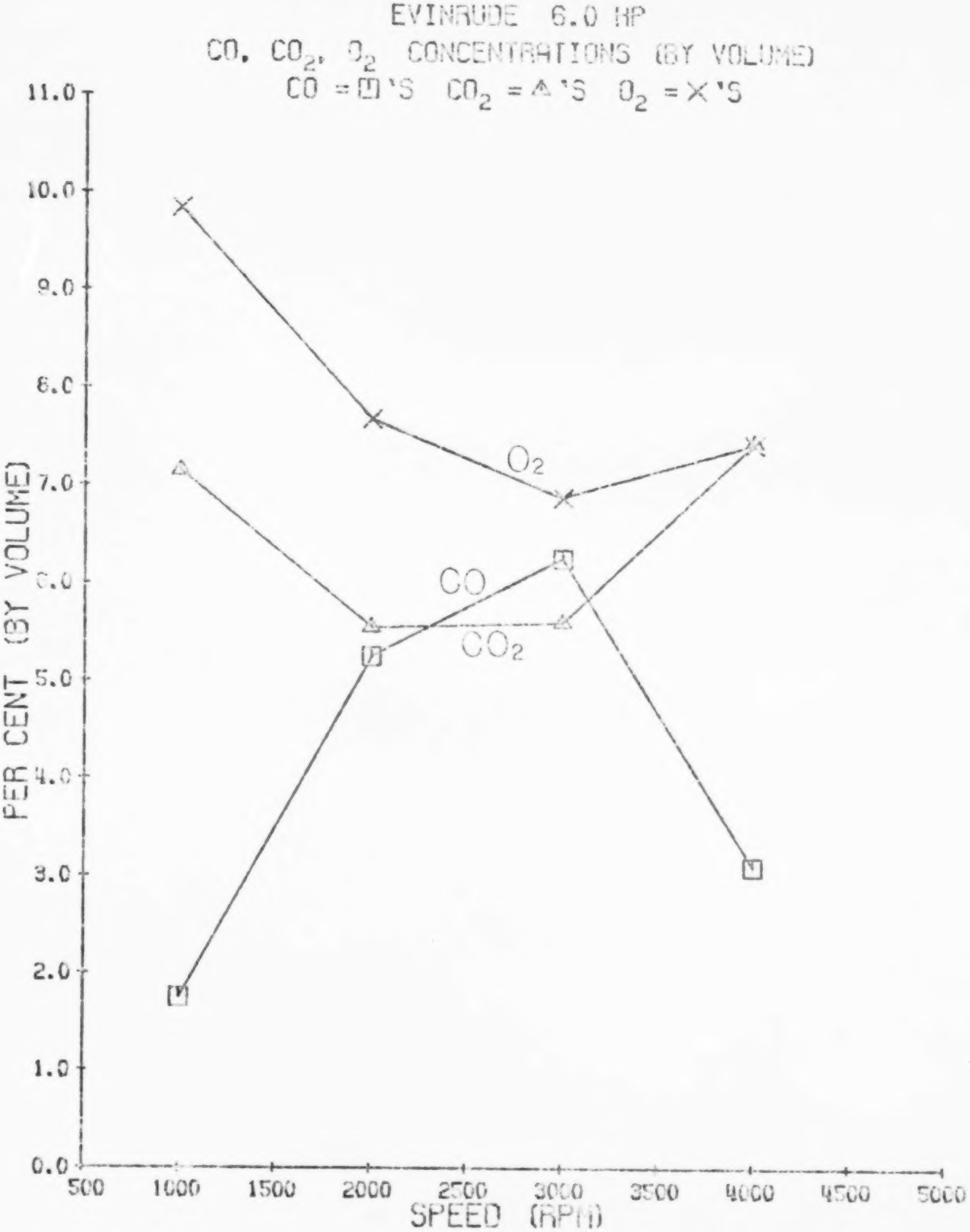

Figure 2 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 6 hp Evinrude

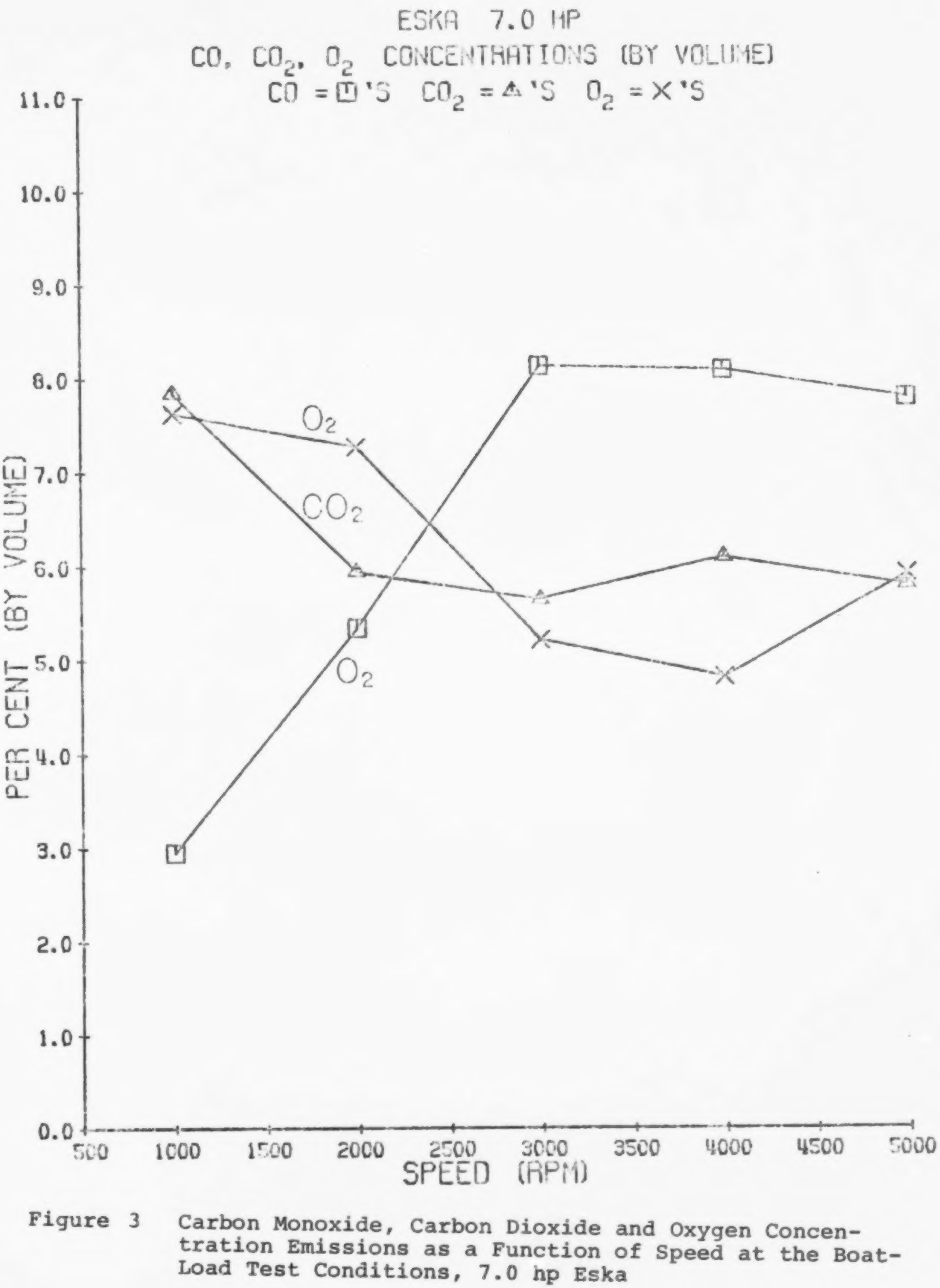

Figure 3 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 7.0 hp Eska

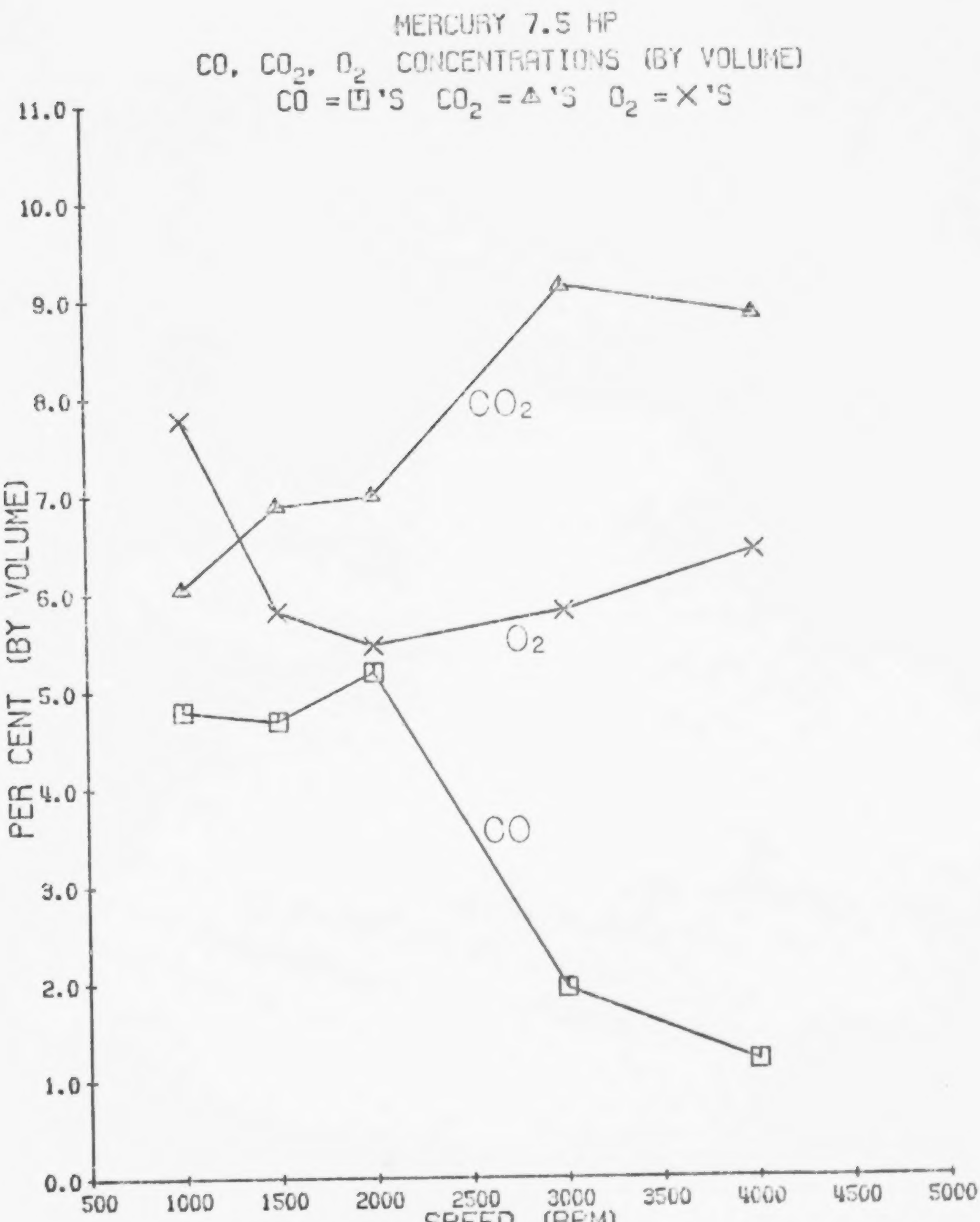

Figure 4 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 7.5 hp Mercury

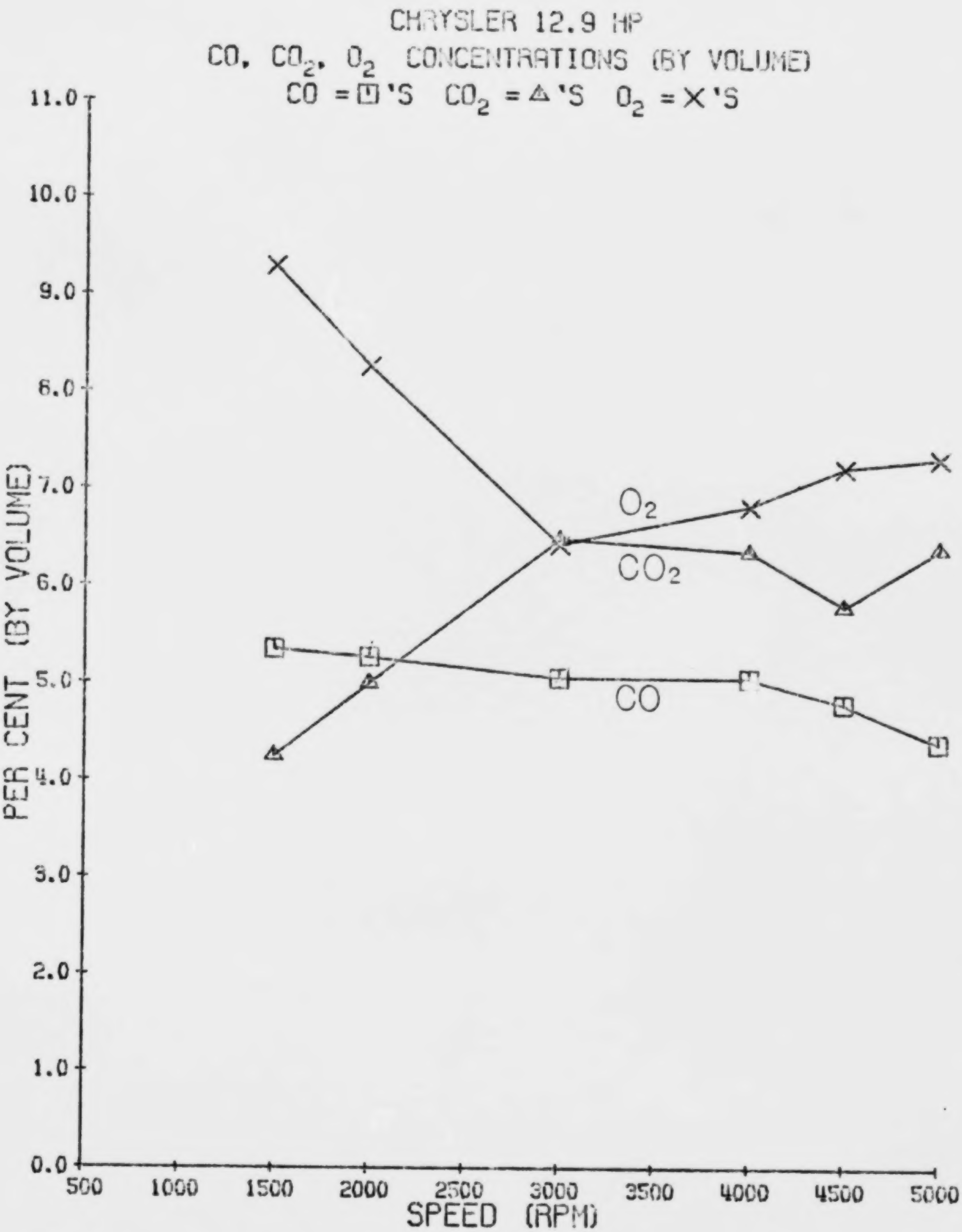

Figure 5 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 12.9 hp Chrysler

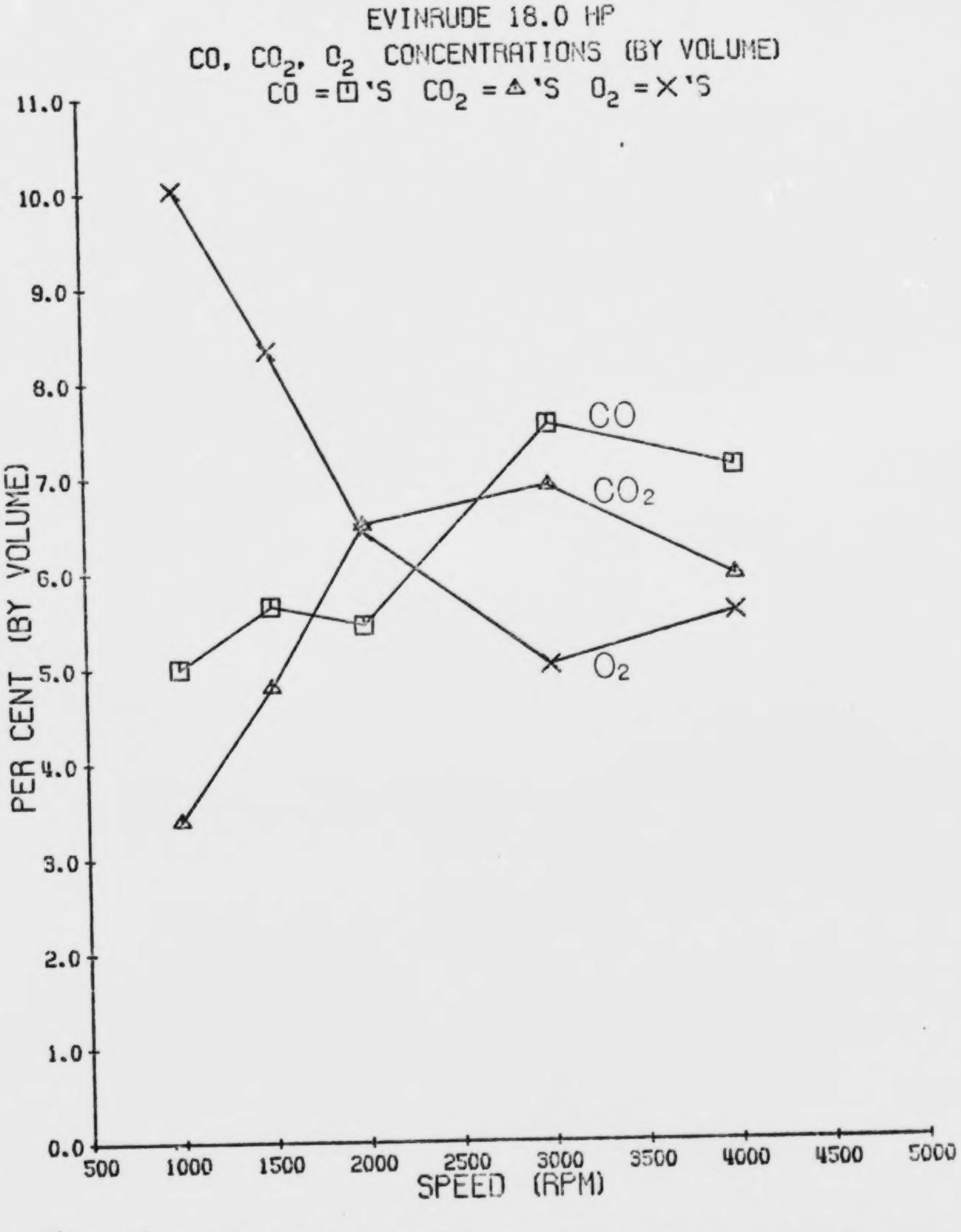

Figure 6 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 18.0 hp Evinrude

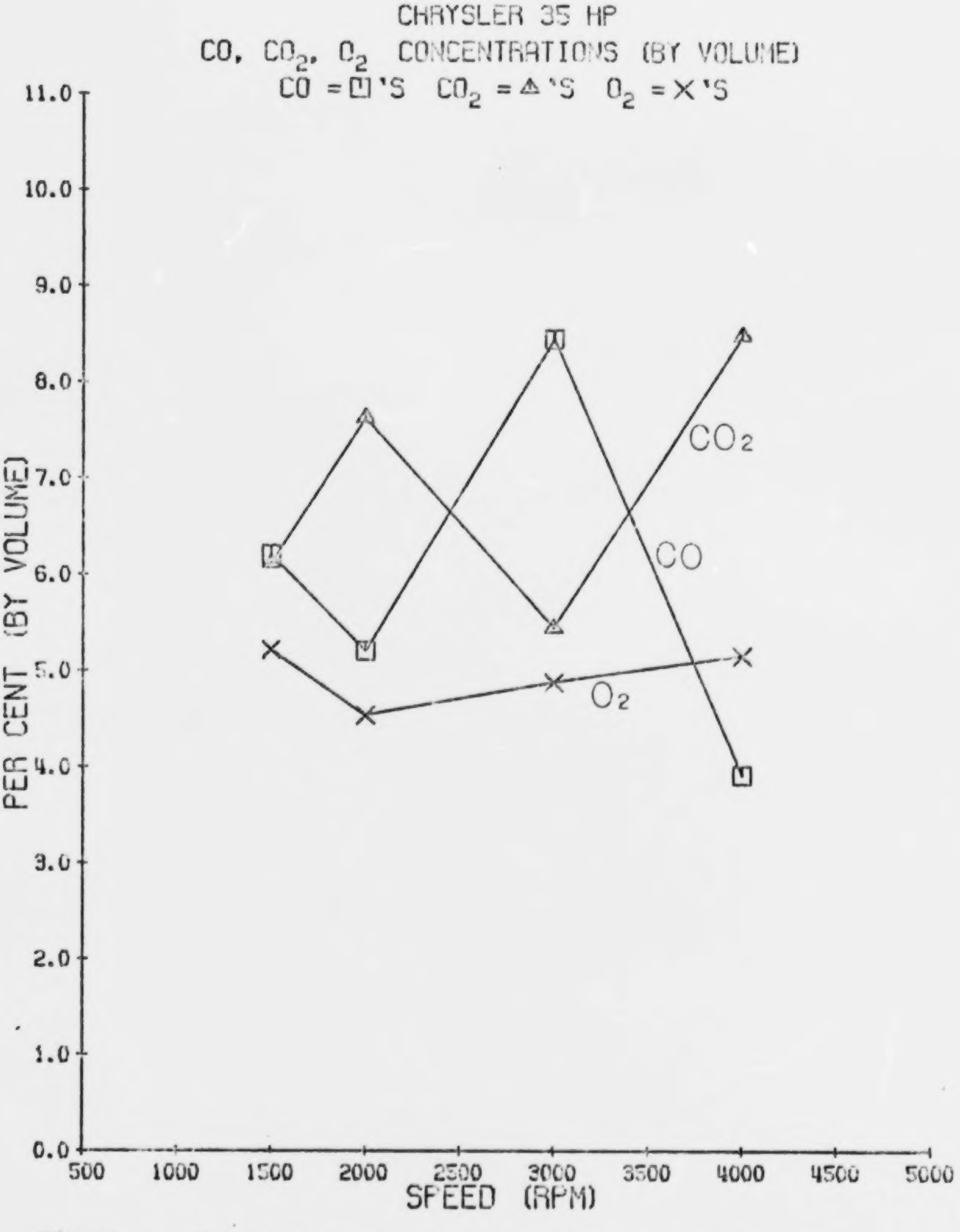

Figure 7 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 35 hp Chrysler

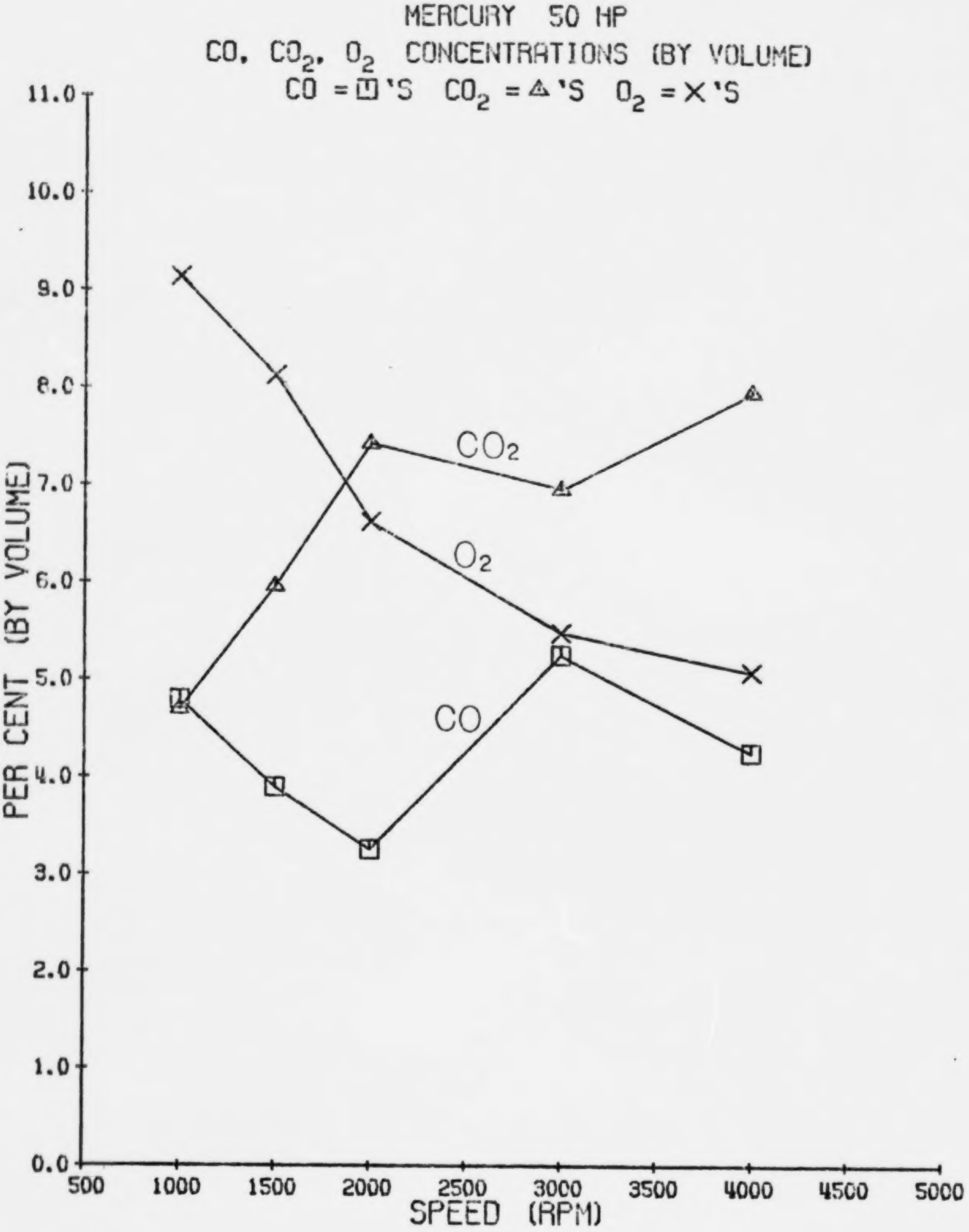

Figure 8 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 50 hp Mercury

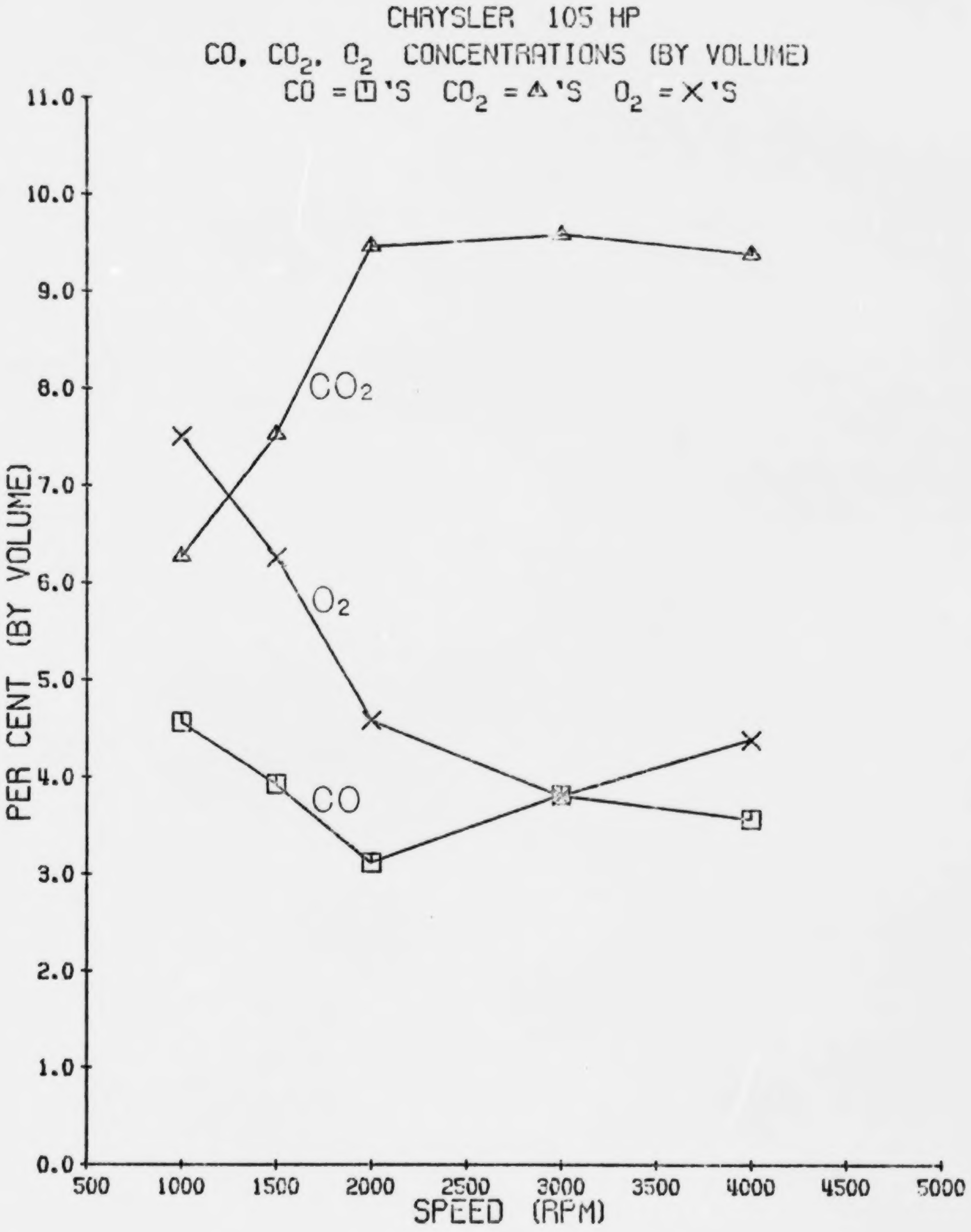

Figure 9 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 105 hp Chrysler

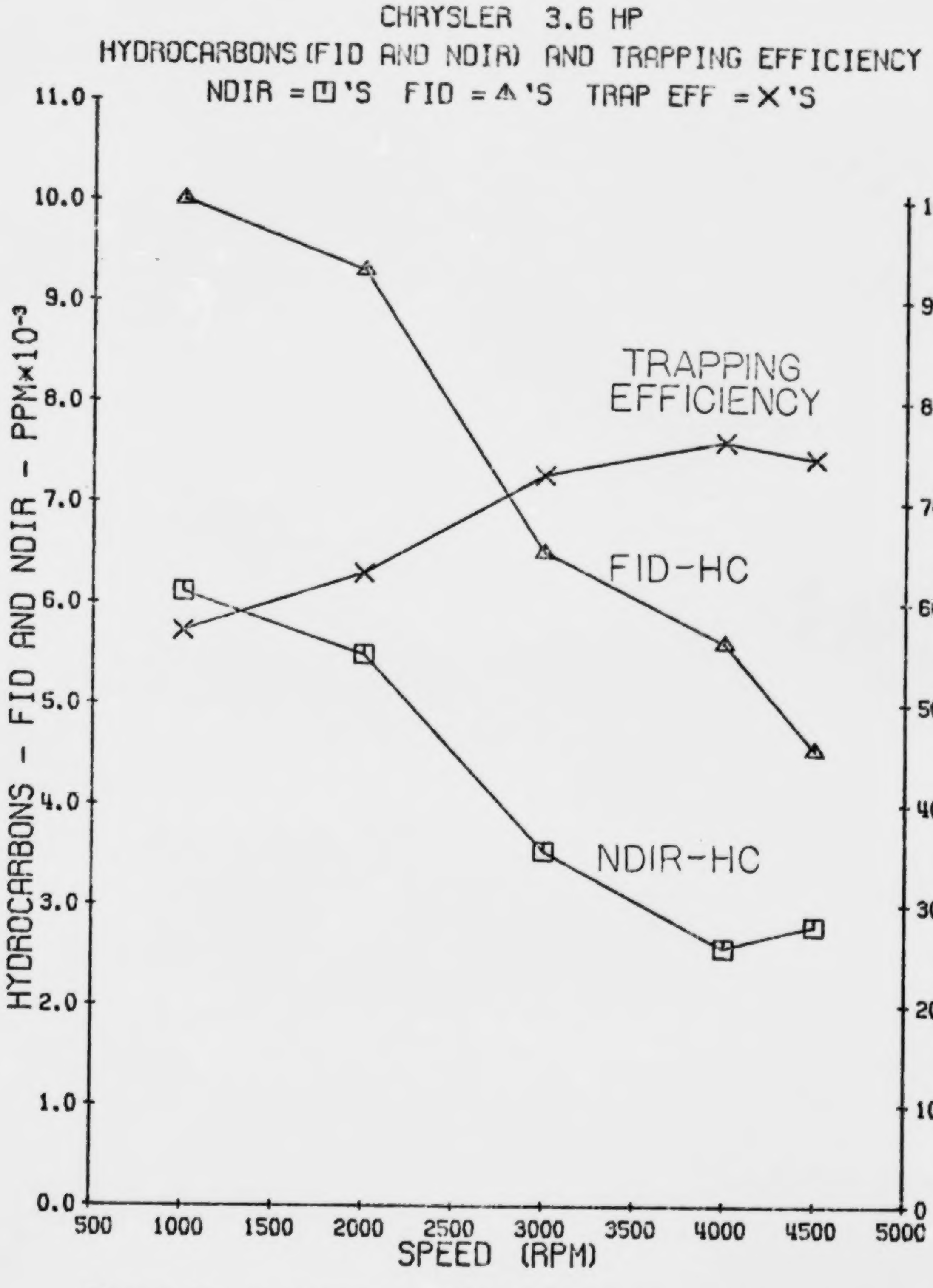

Figure 10 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 3.6 hp Chrysler

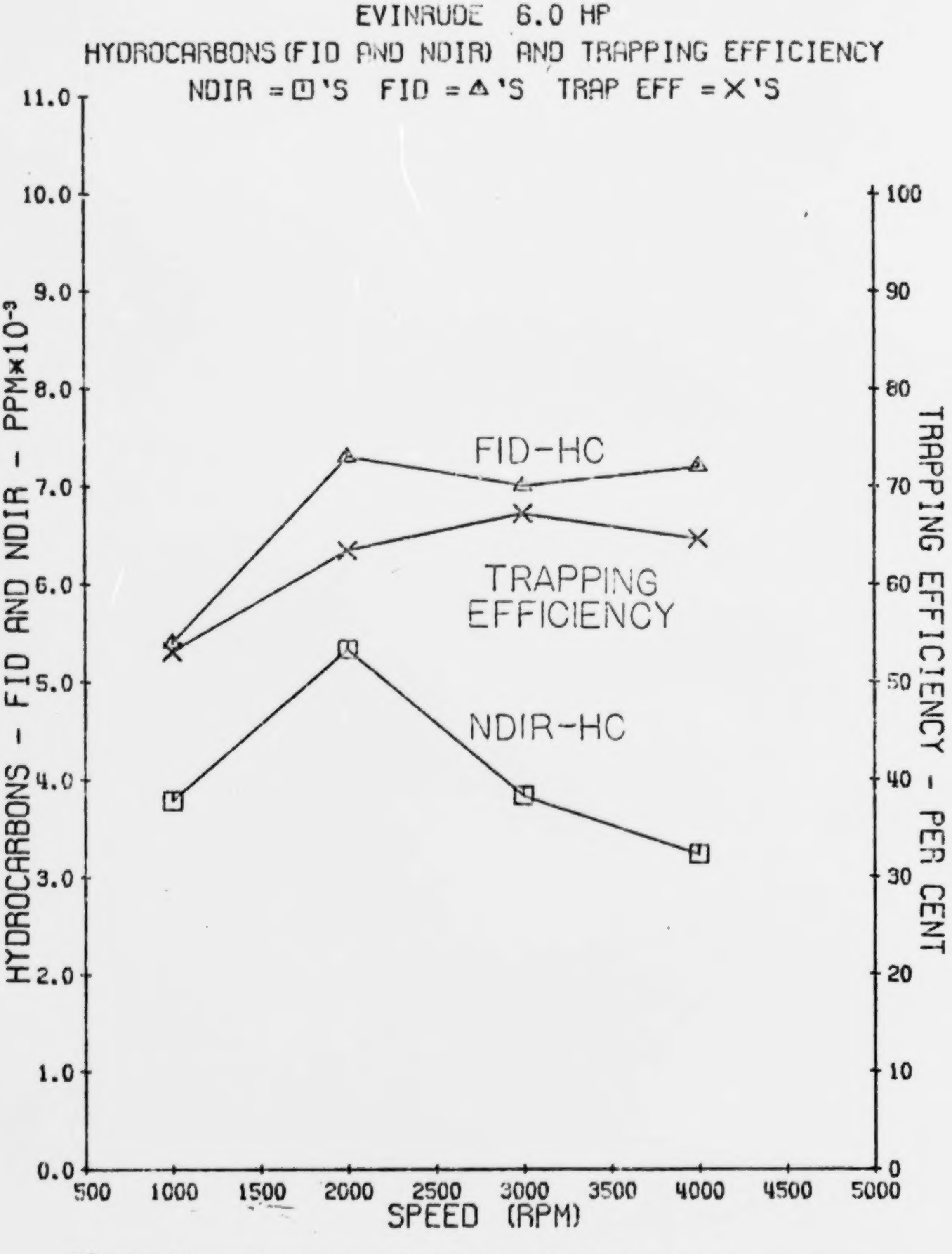

Figure 11 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 6.0 hp Evinrude

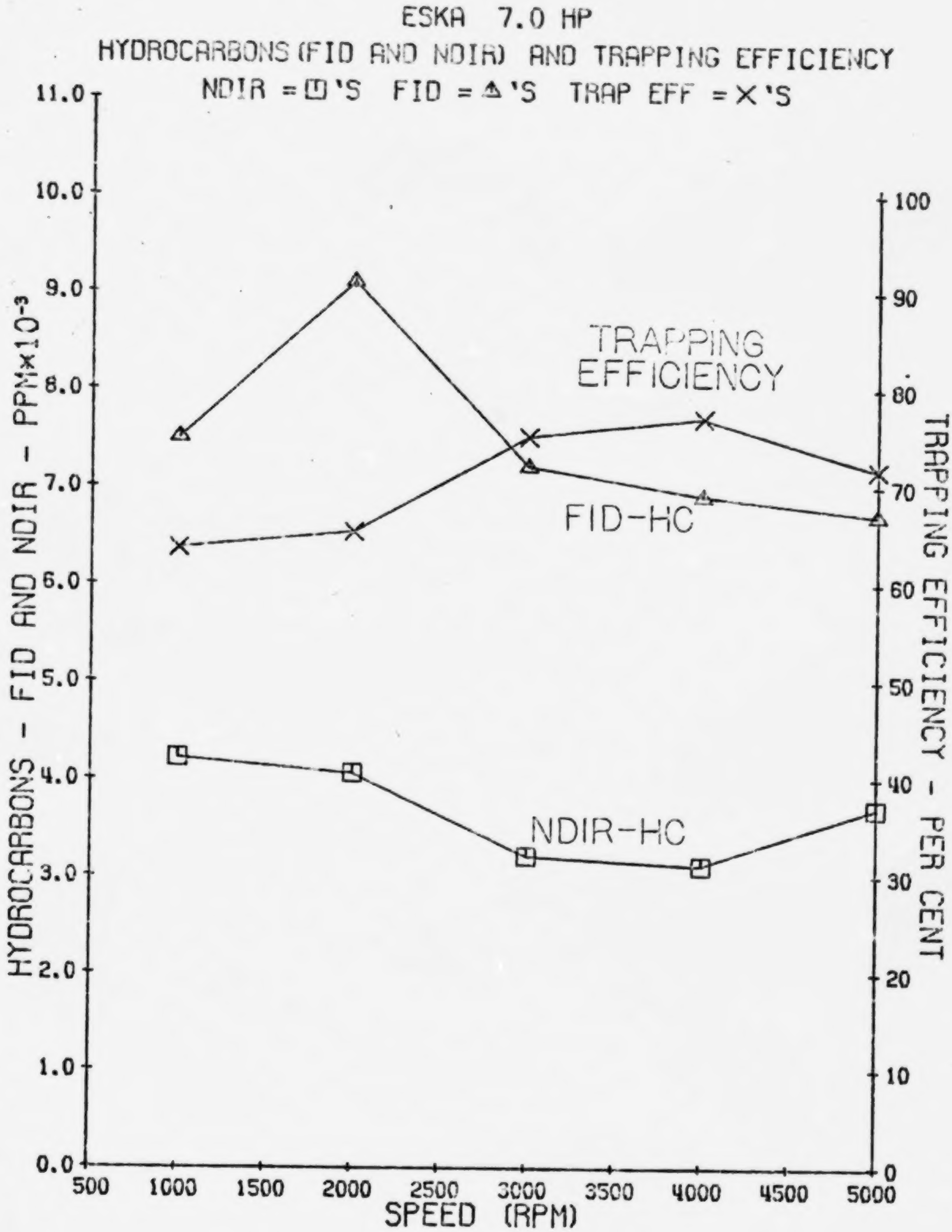

Figure 12 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 7.0 hp Eska

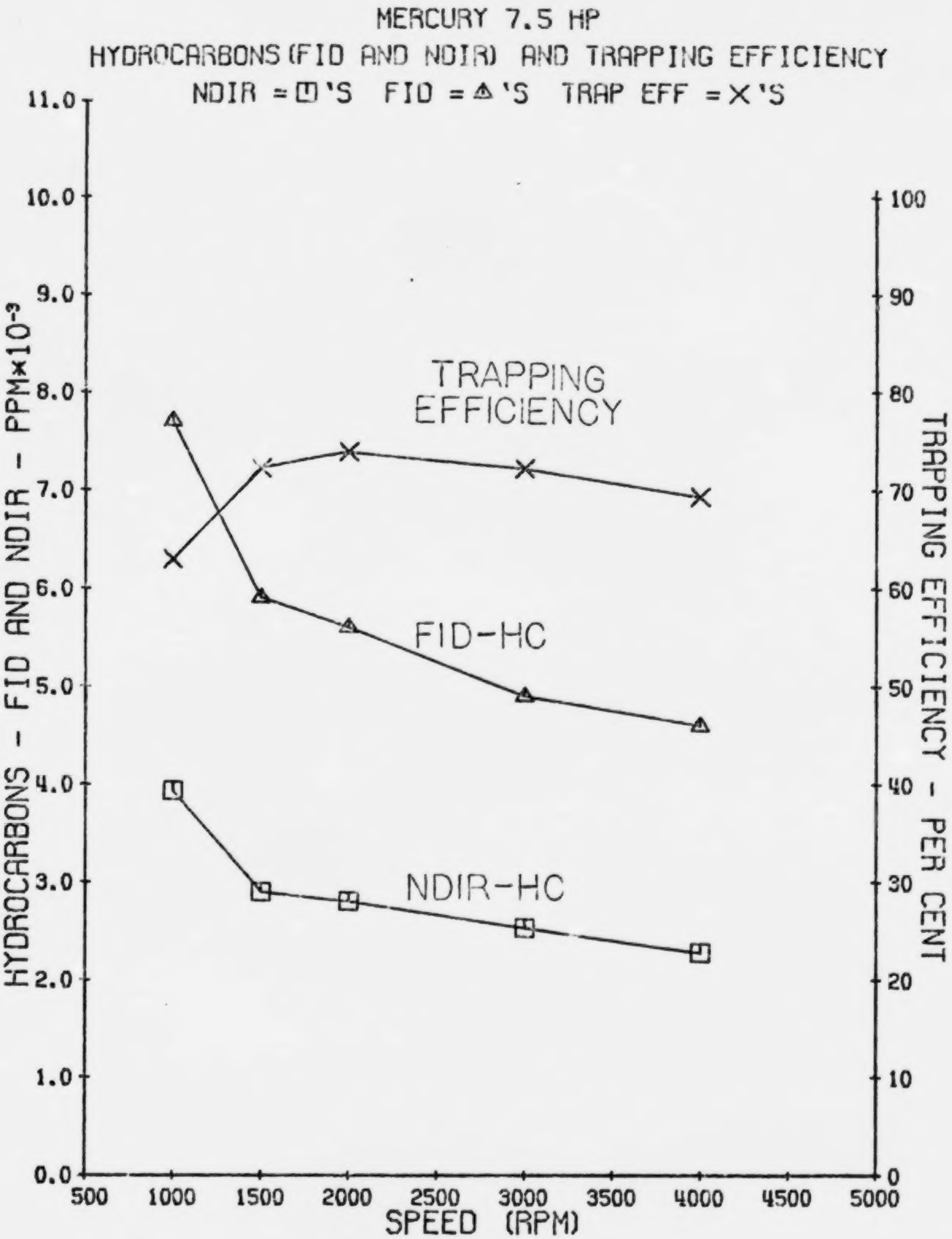

Figure 13 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 7.5 hp Mercury

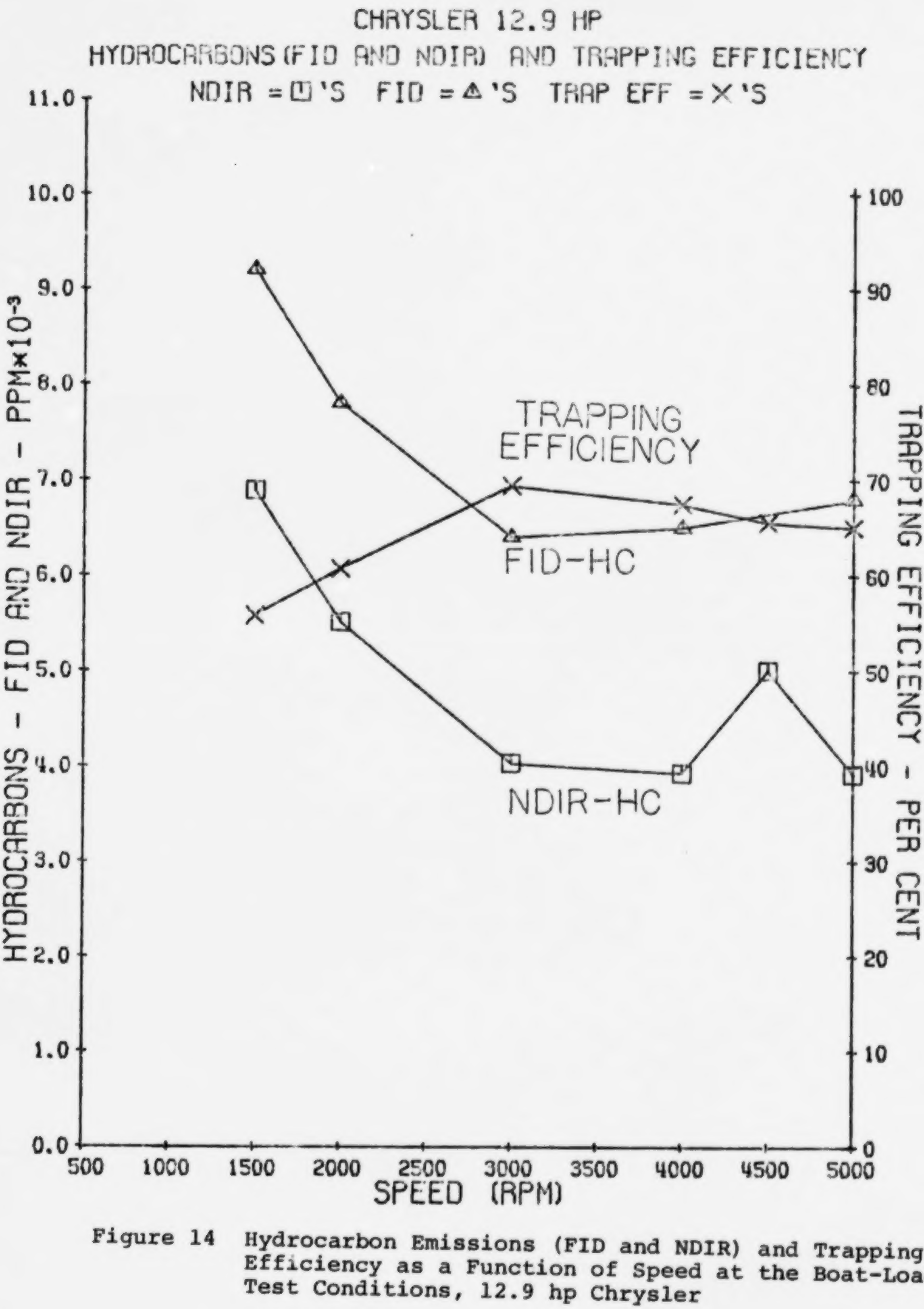

Figure 14 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 12.9 hp Chrysler

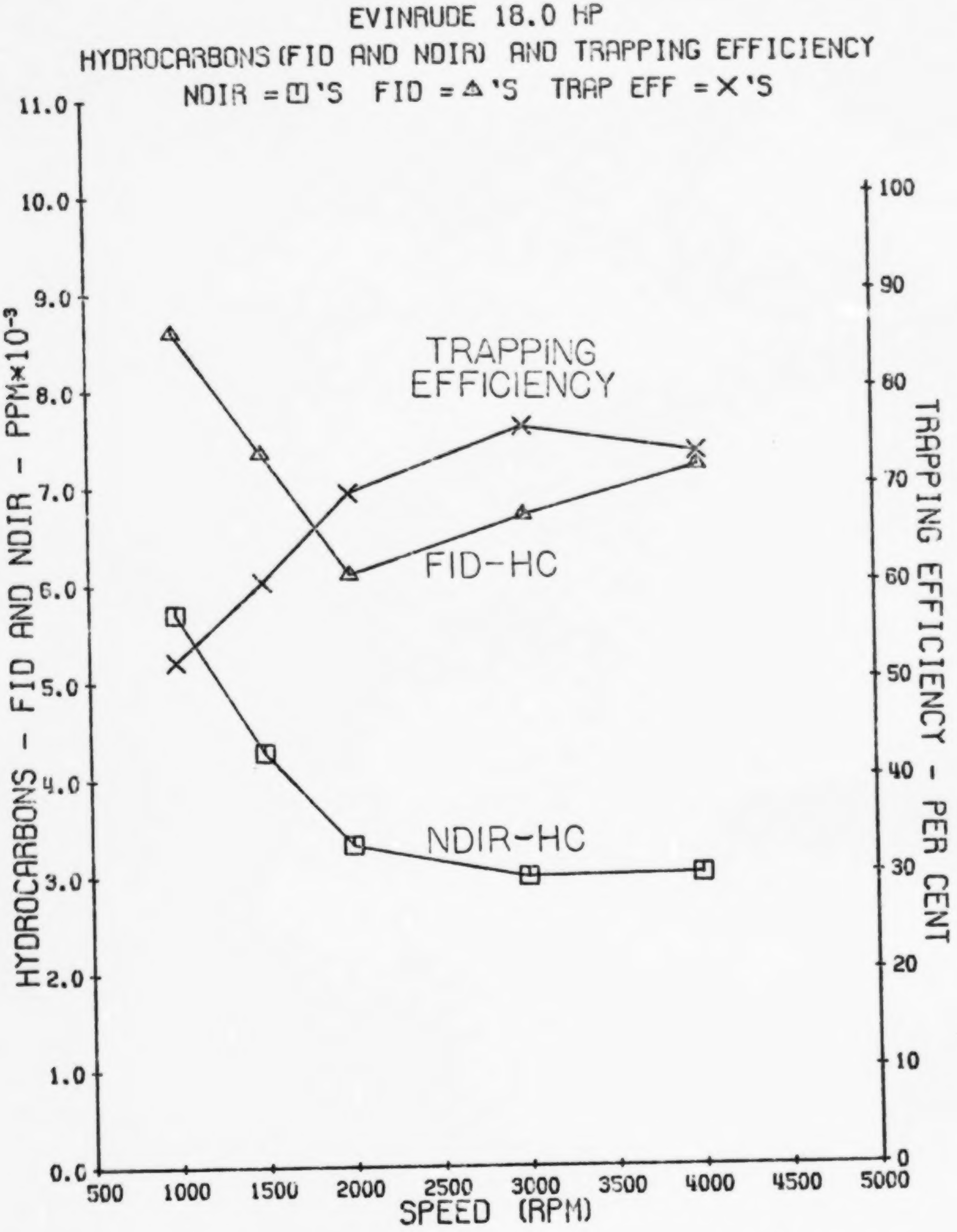

Figure 15 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 18.0 hp Evinrude

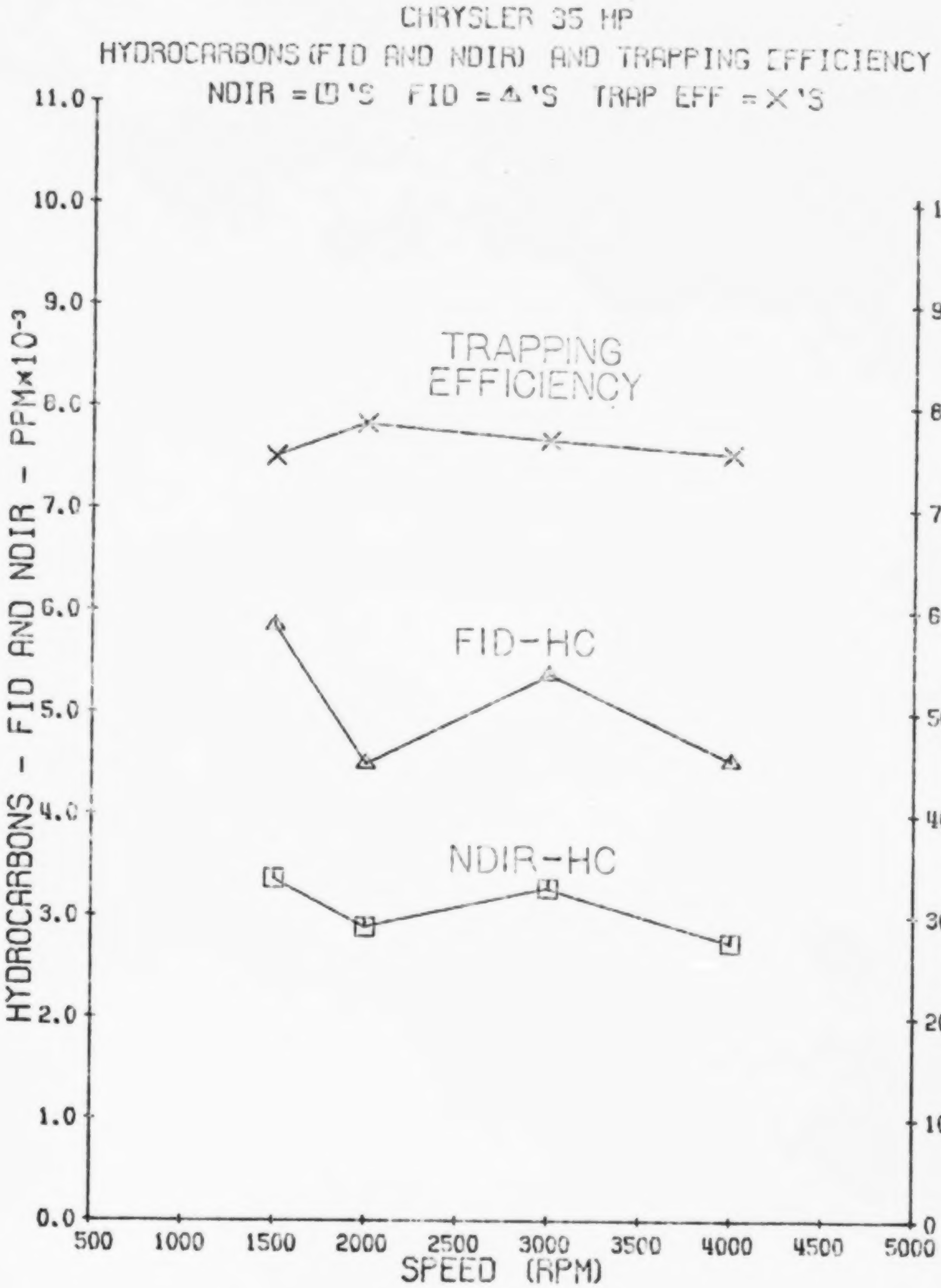

Figure 16 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 35 hp Chrysler

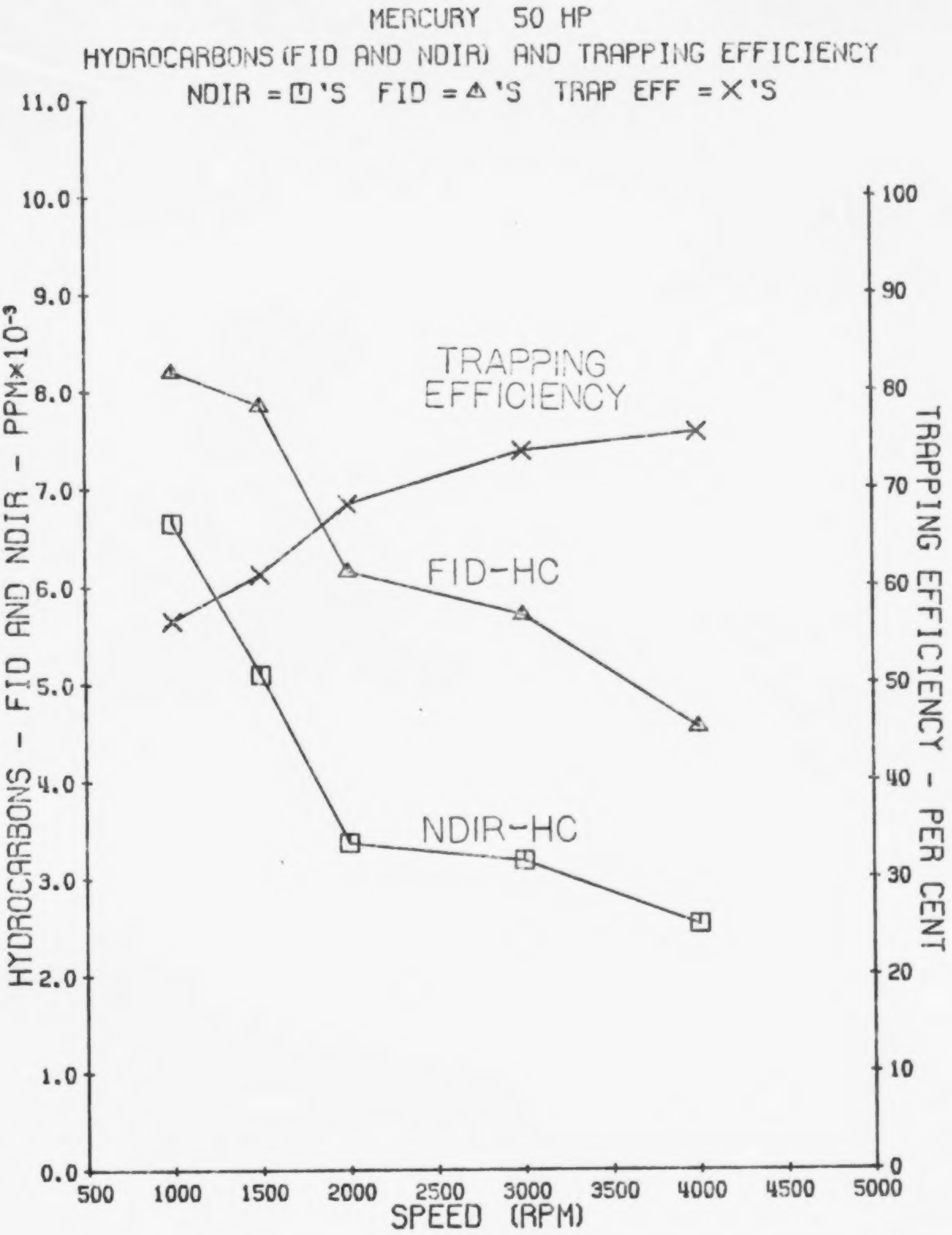

Figure 17 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 50 hp Mercury

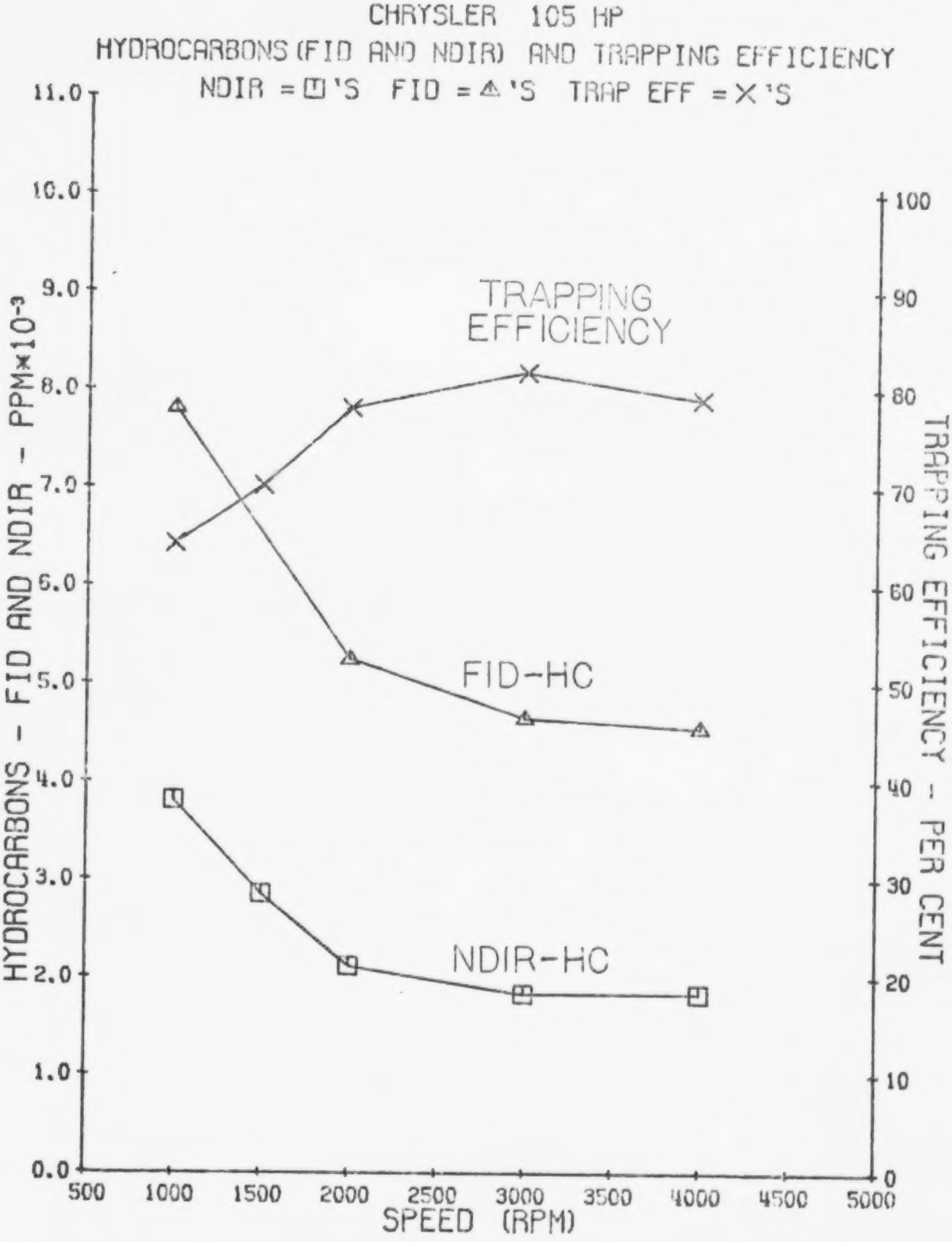

Figure 18 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 105 hp Chrysler

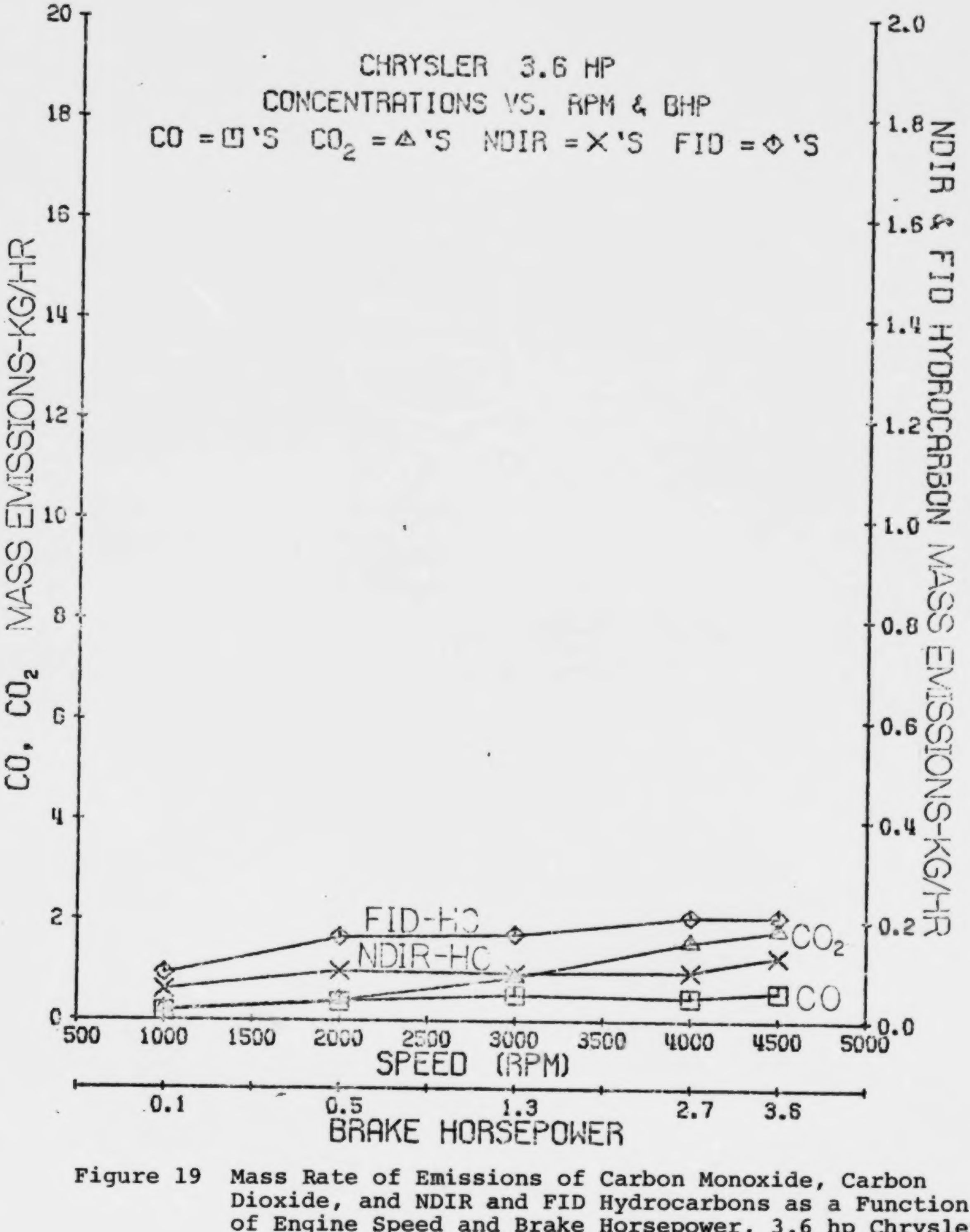

Figure 19 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 3.6 hp Chrysler Engine

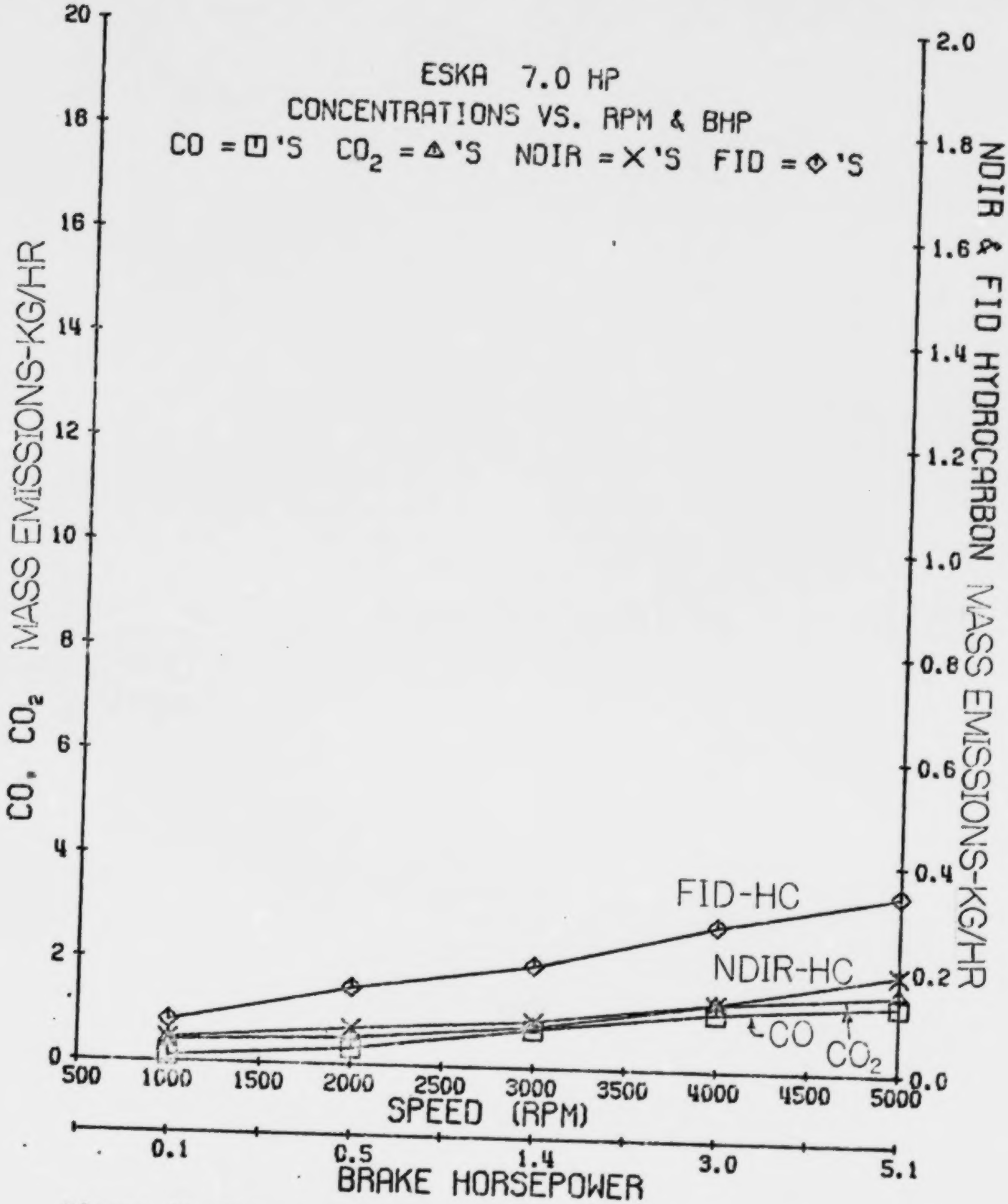

Figure 20 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 7.0 hp Eska Engine

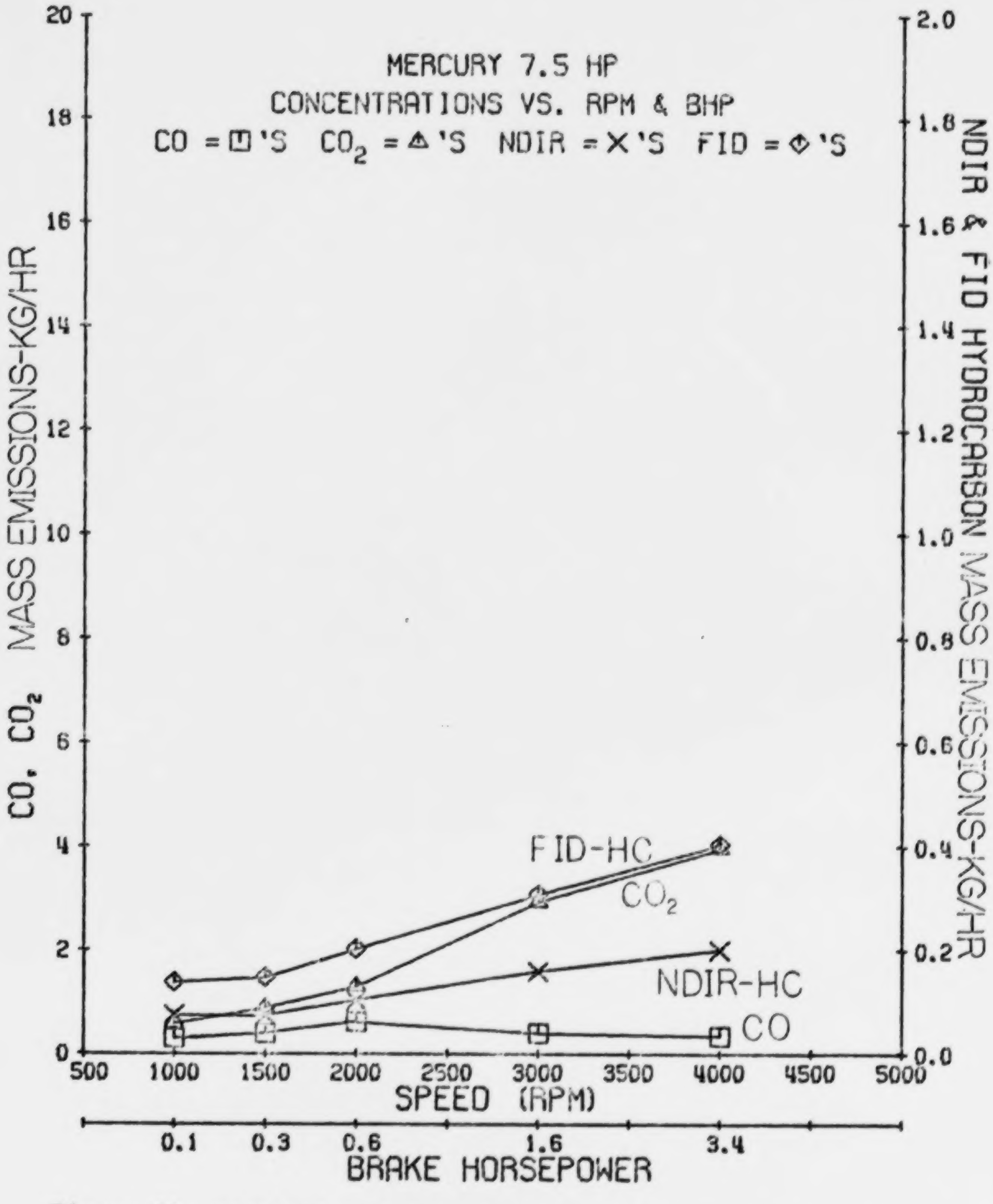

Figure 21 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 7.5 Mercury Engine

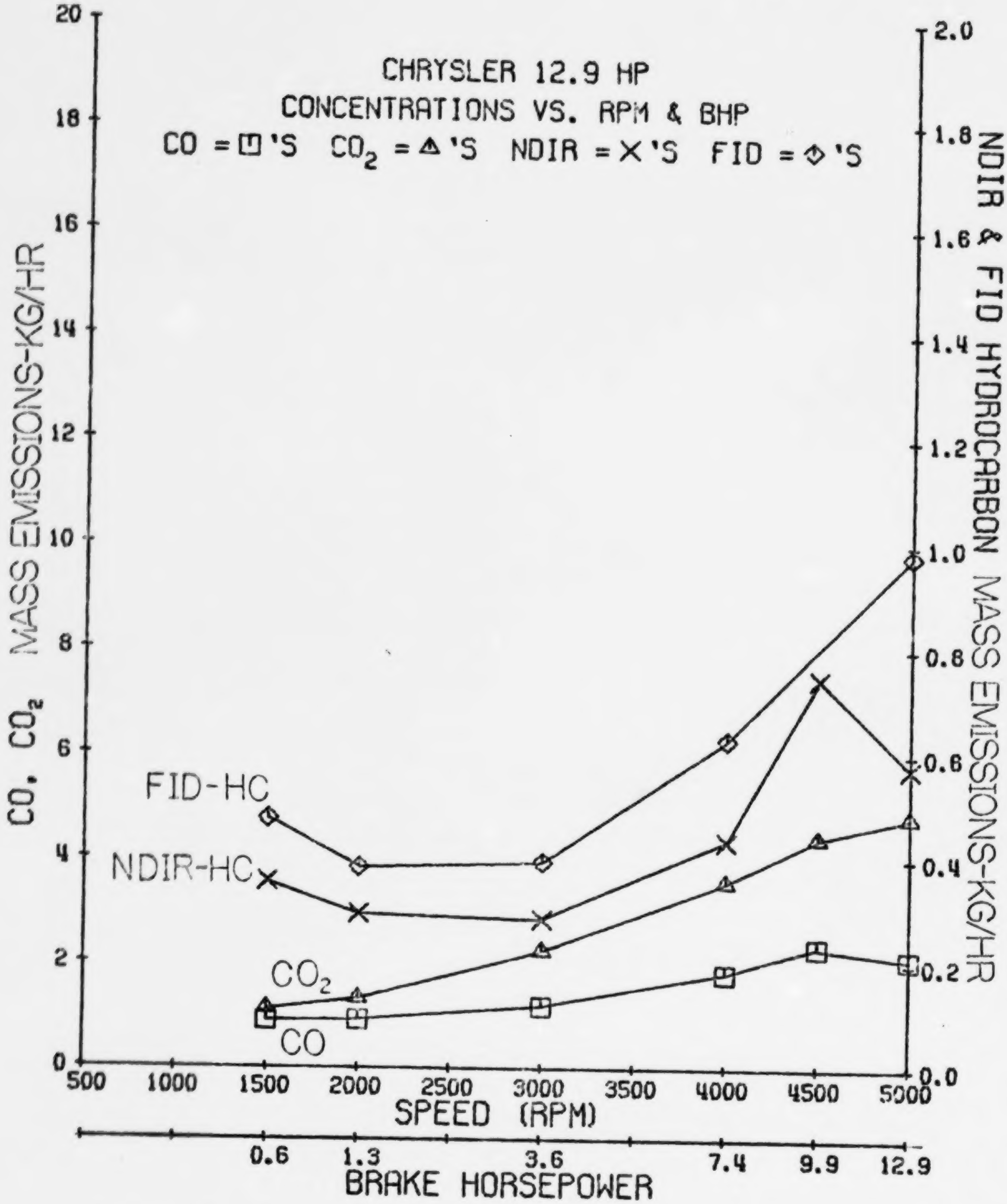

Figure 22 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 12.9 Chrysler Engine

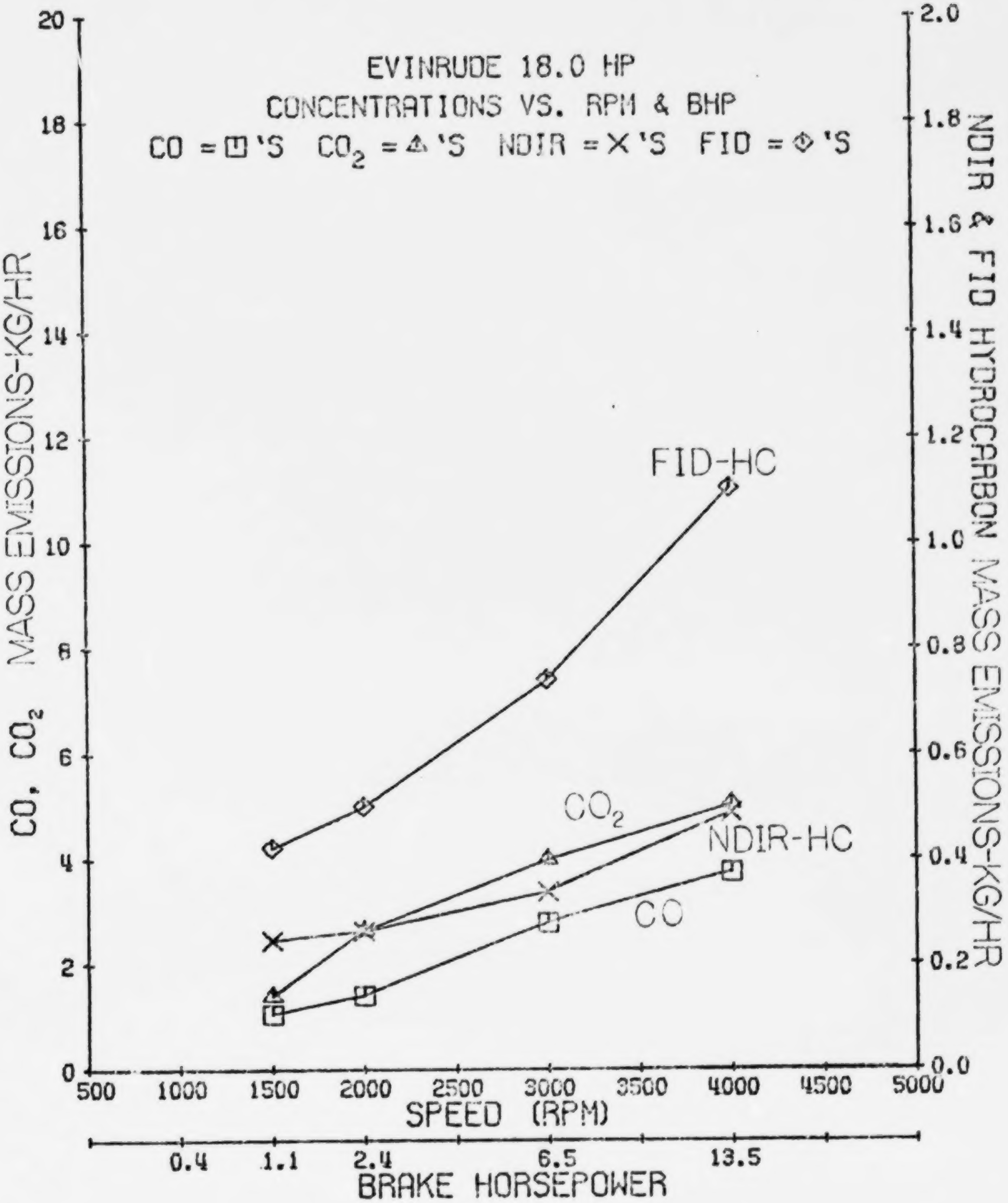

Figure 23 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 18.0 hp Evinrude Engine

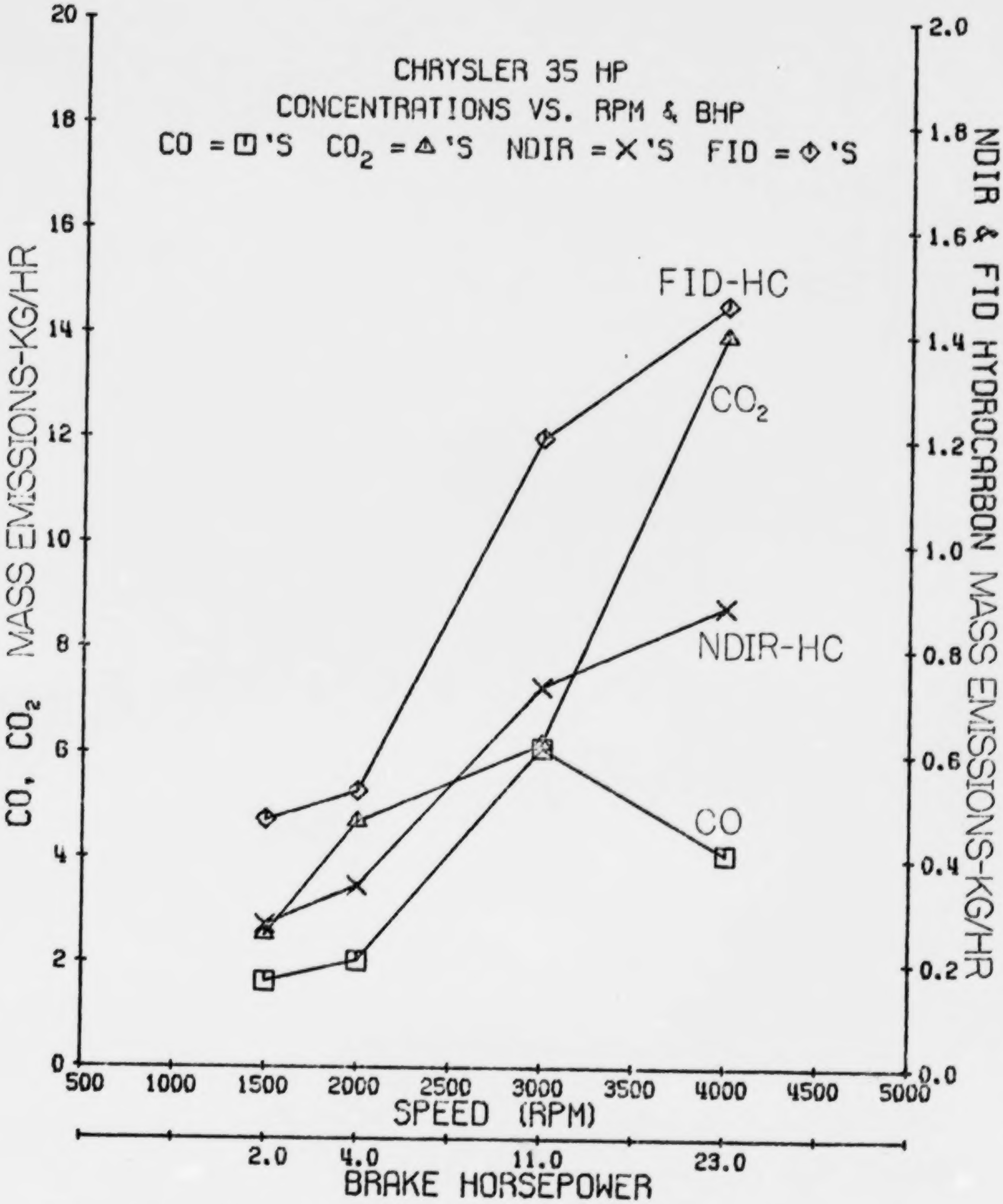

Figure 24 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 35 hp Chrysler Engine

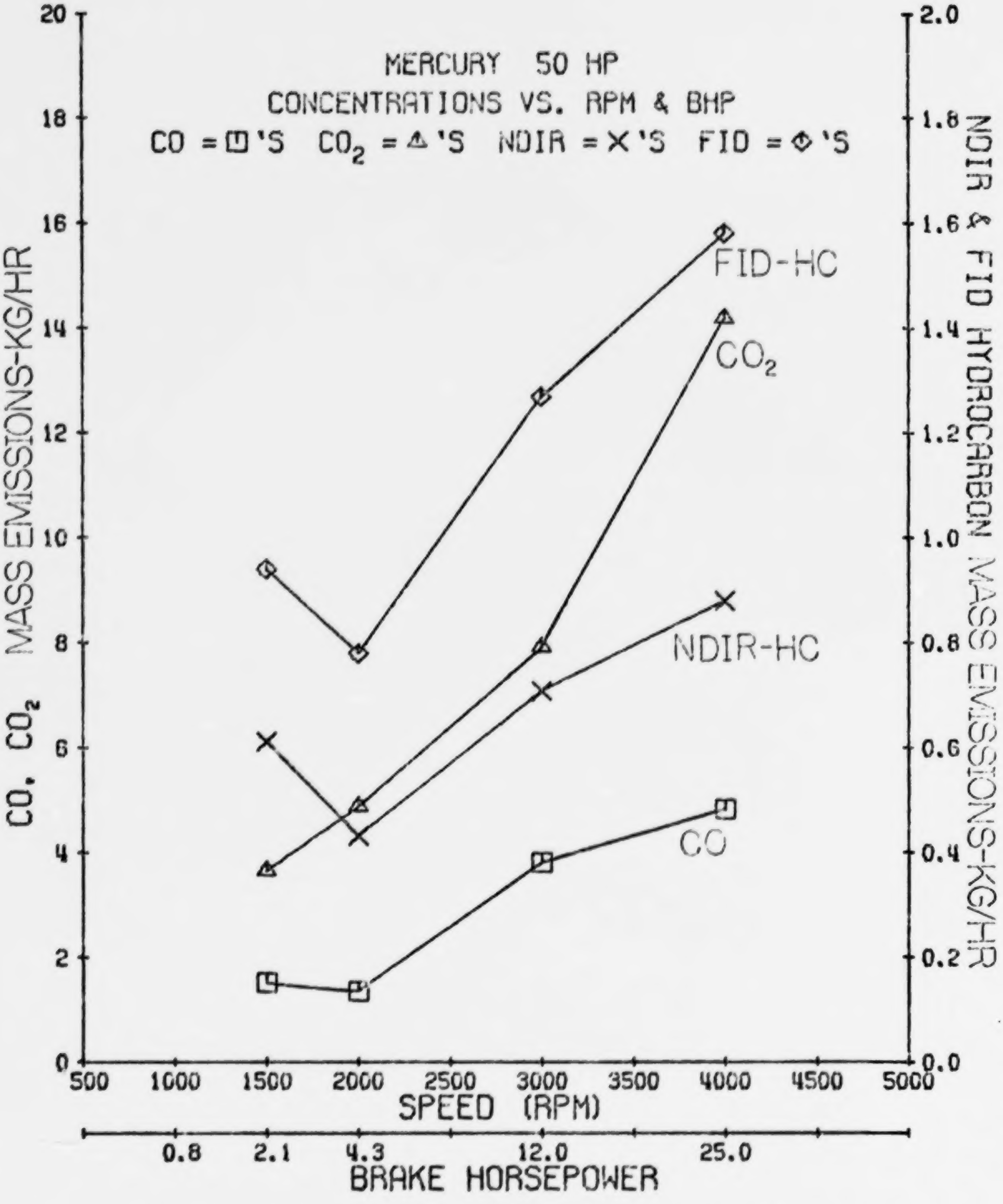

Figure 25 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 50 hp Mercury Engine

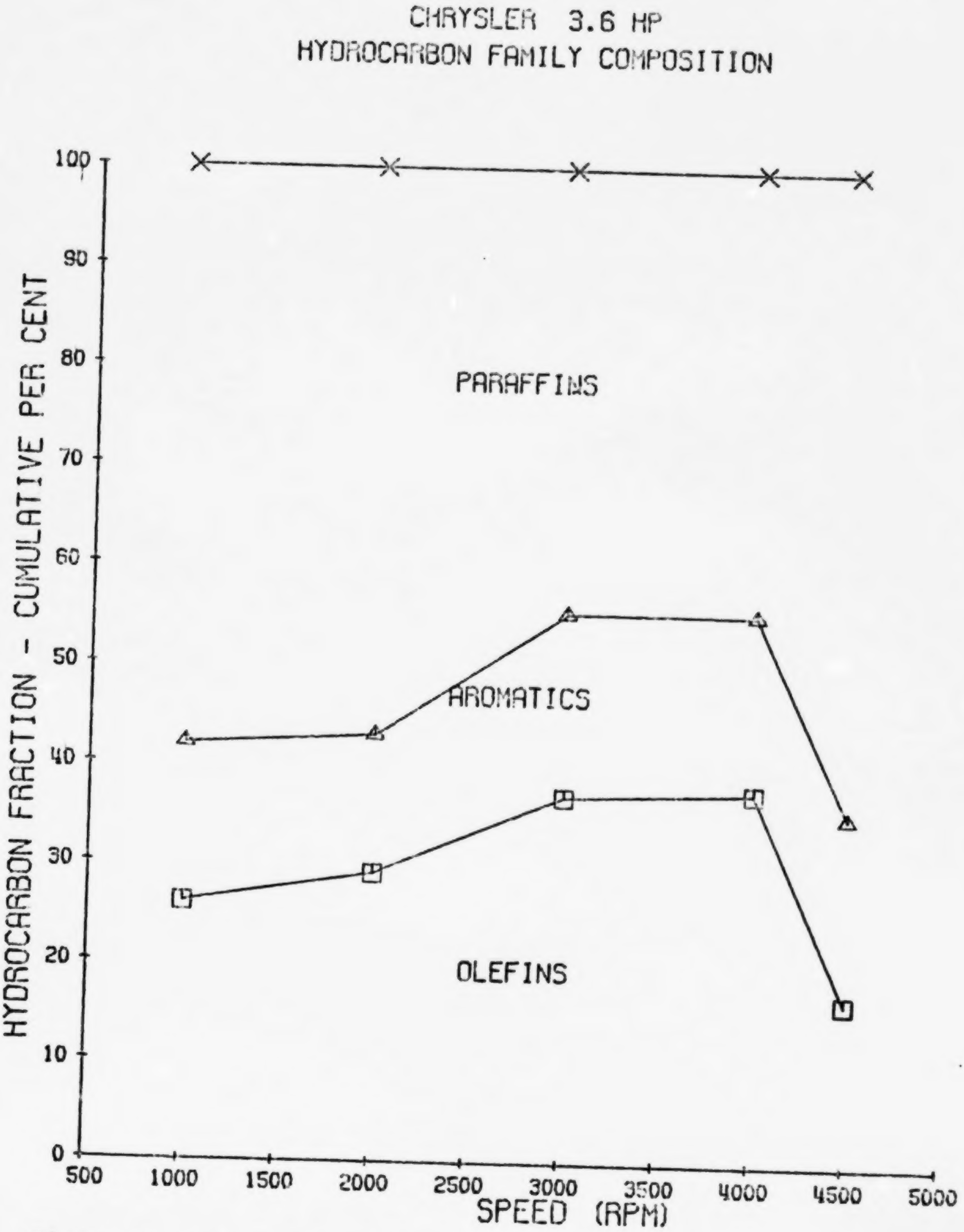

Figure 26 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 3.6 hp Chrysler Engine.

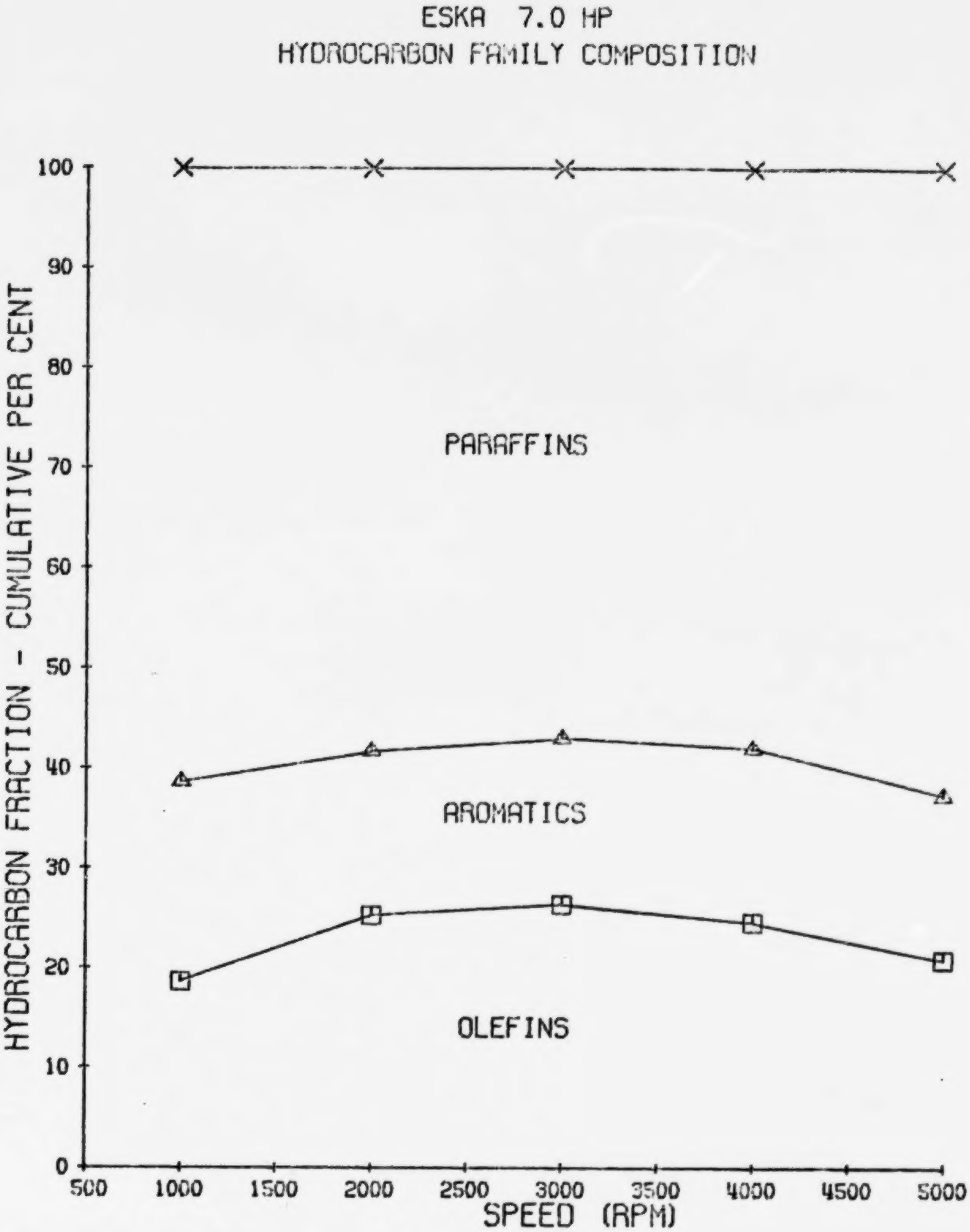

Figure 27 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 7.0 hp Eska Engine

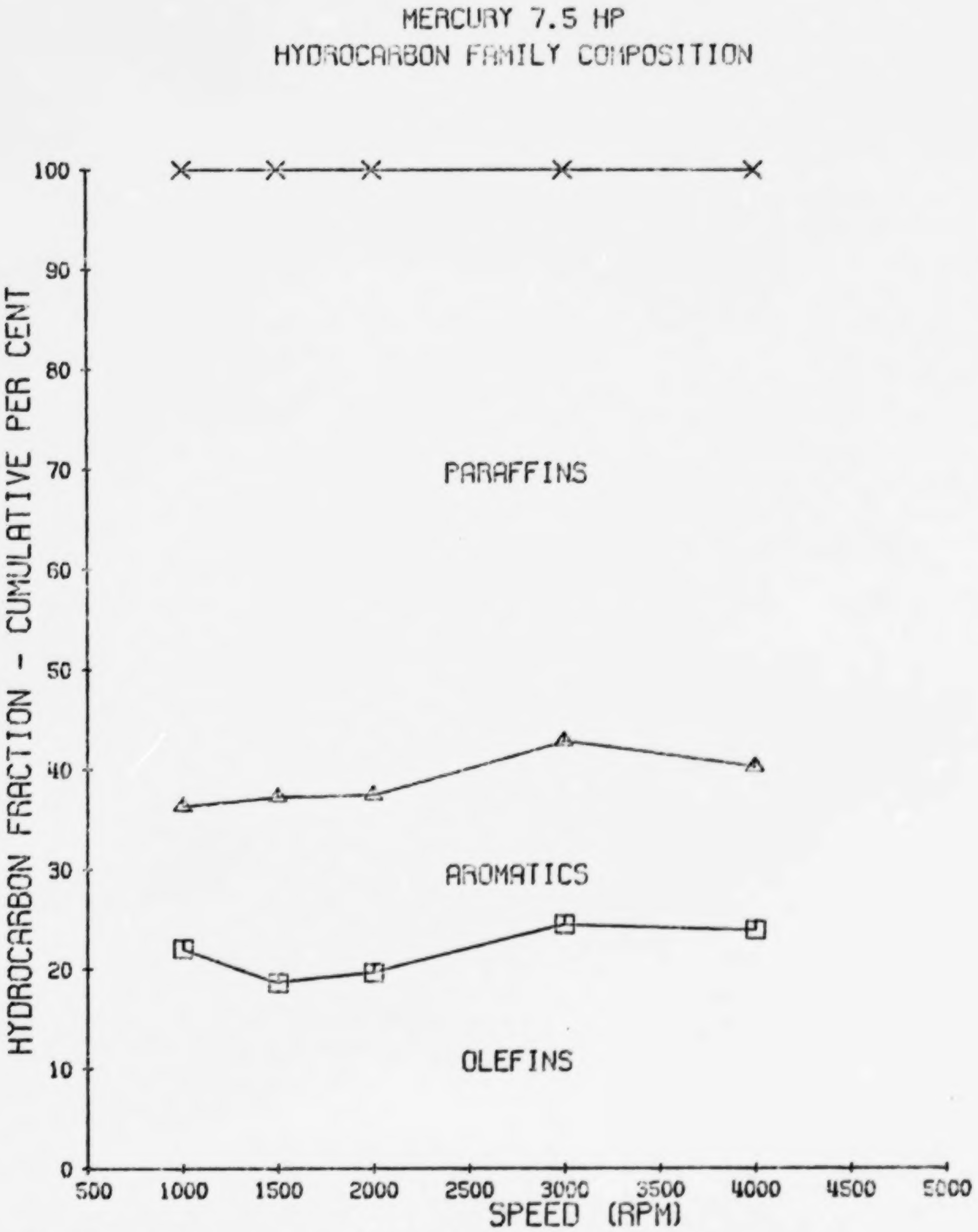

Figure 28 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 7.5 hp Mercury Engine

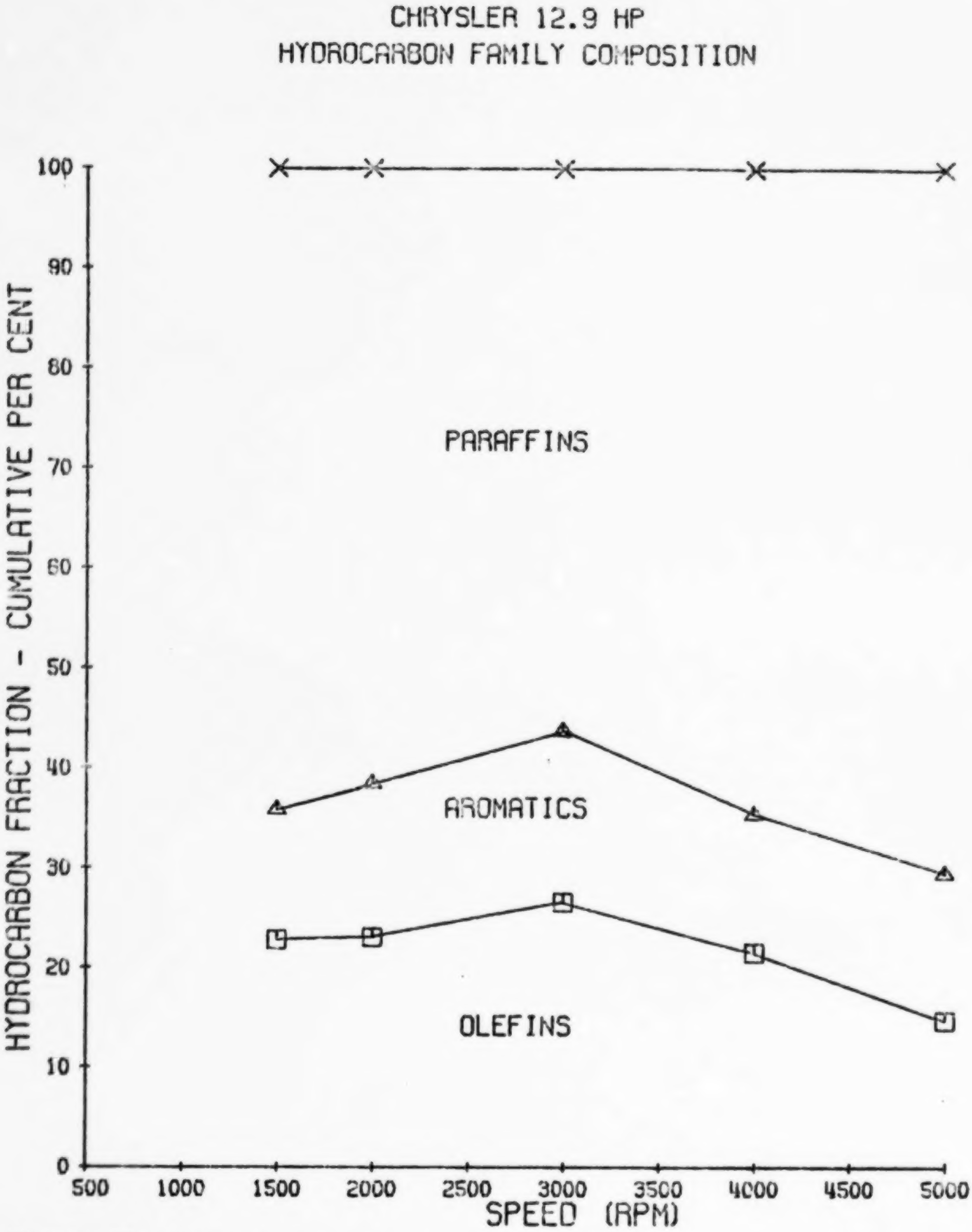

Figure 29 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 12.9 hp Chrysler Engine

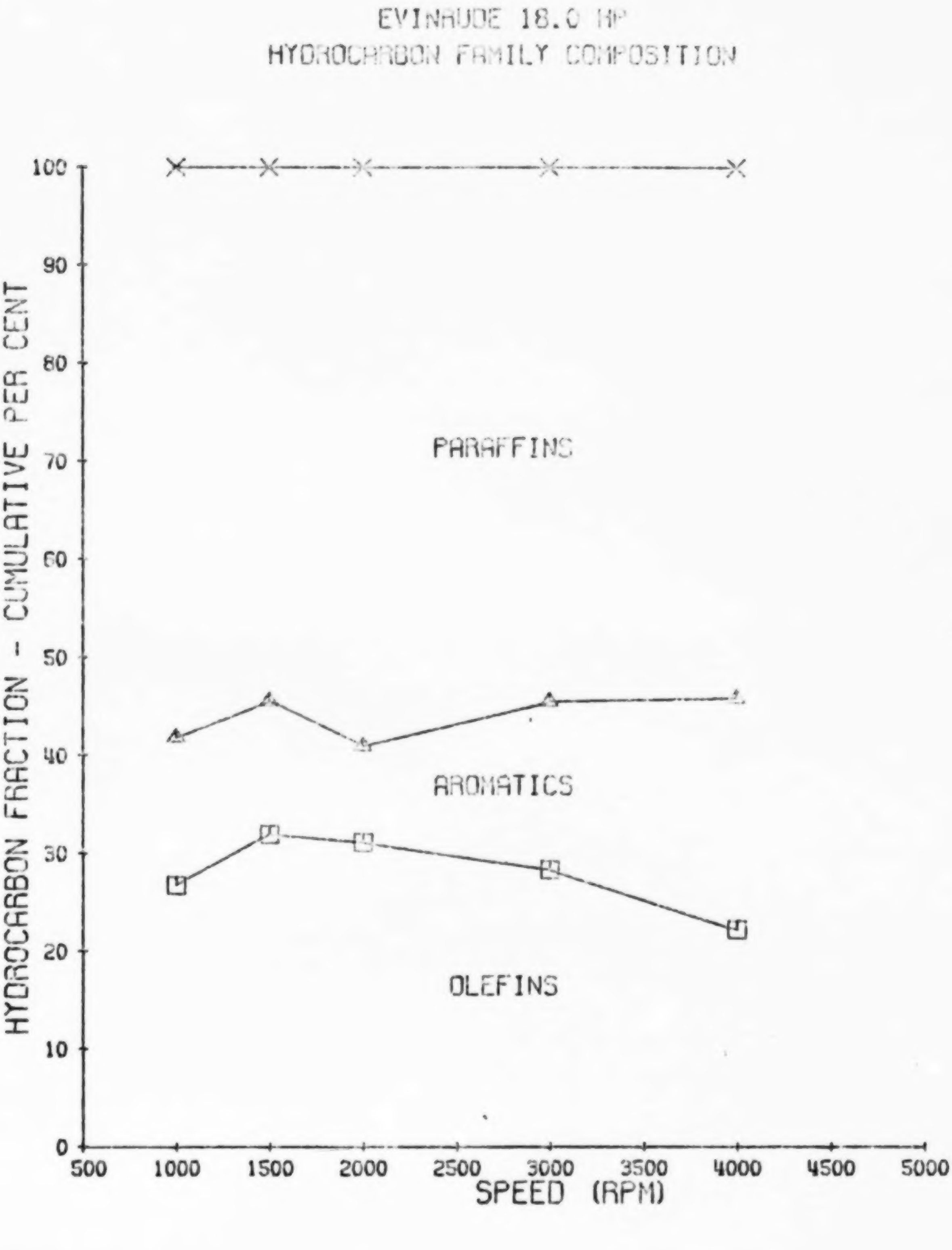

Figure 30 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 18.0 hp Evinrude Engine

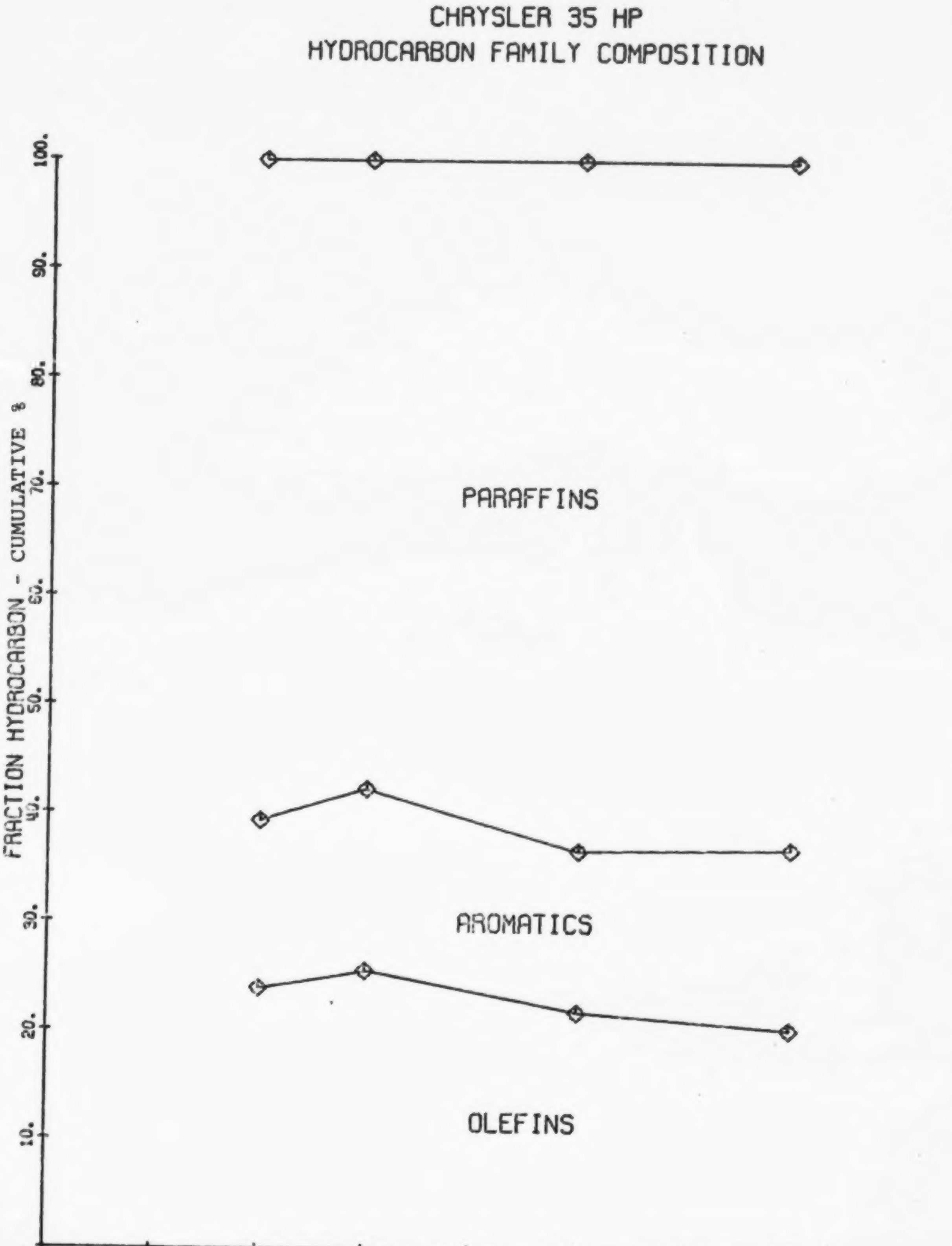

Figure 31 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 35 hp Chrysler Engine

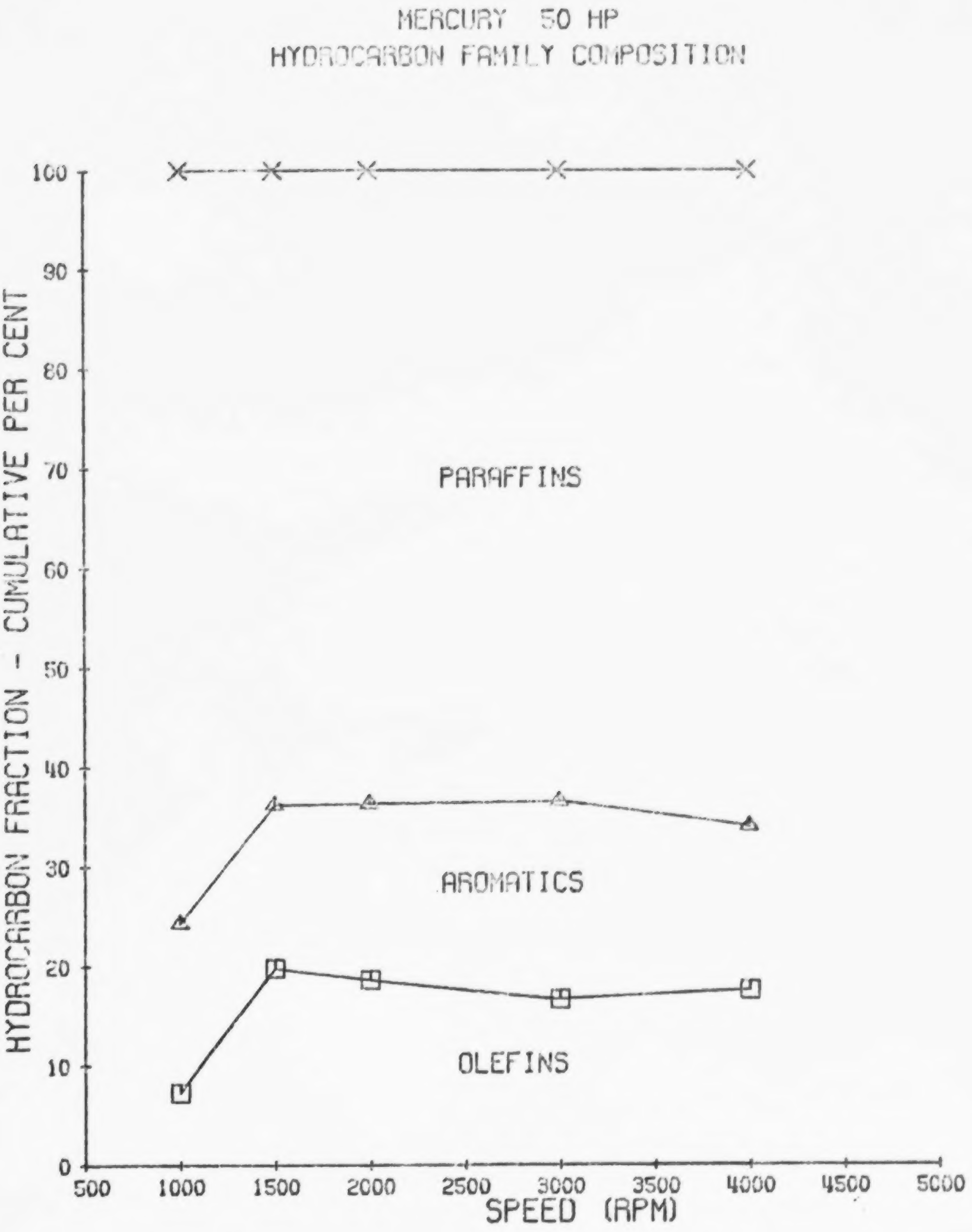

Figure 32 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 50 hp Mercury

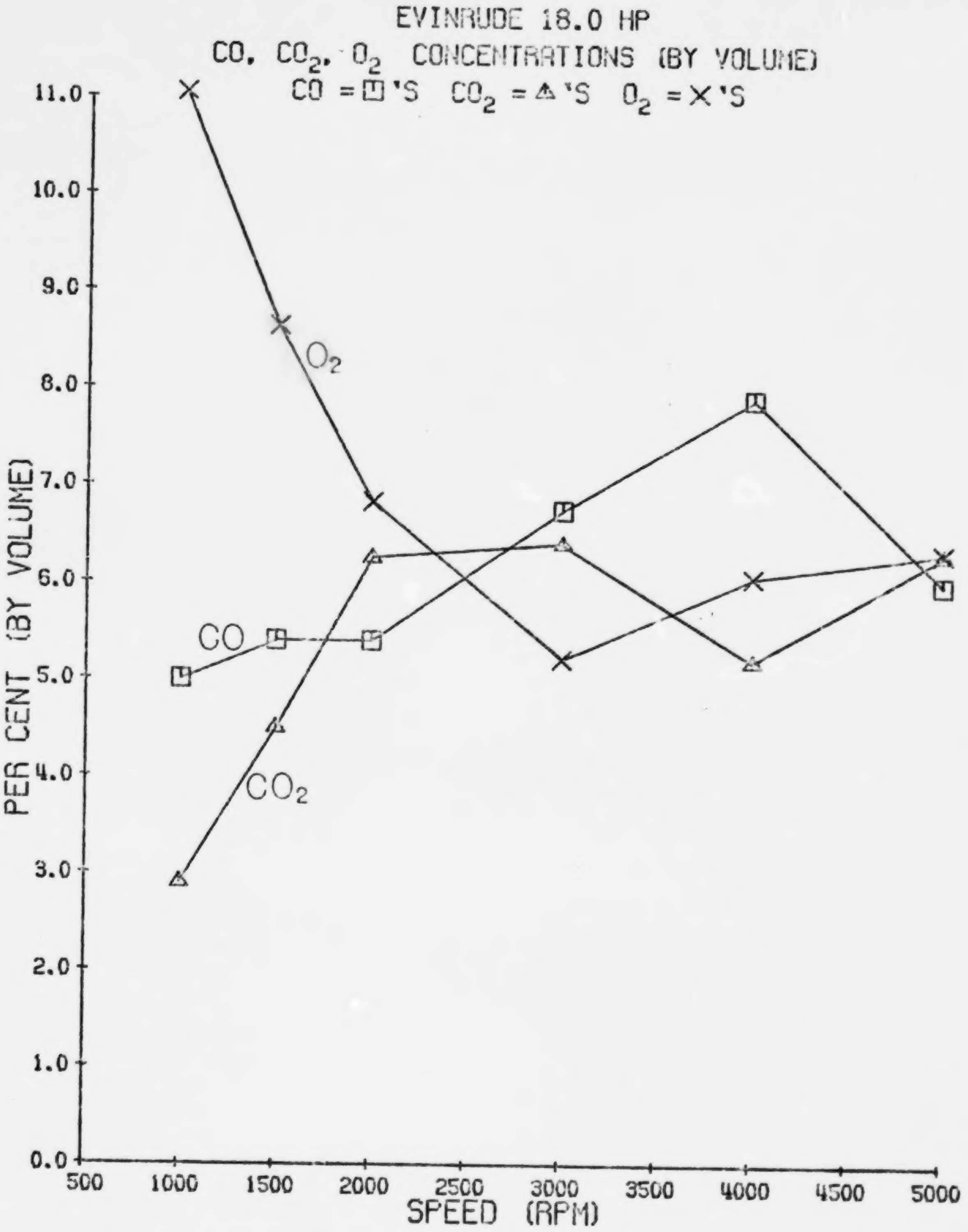

Figure 33 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 18.0 hp Evinrude Drained Engine

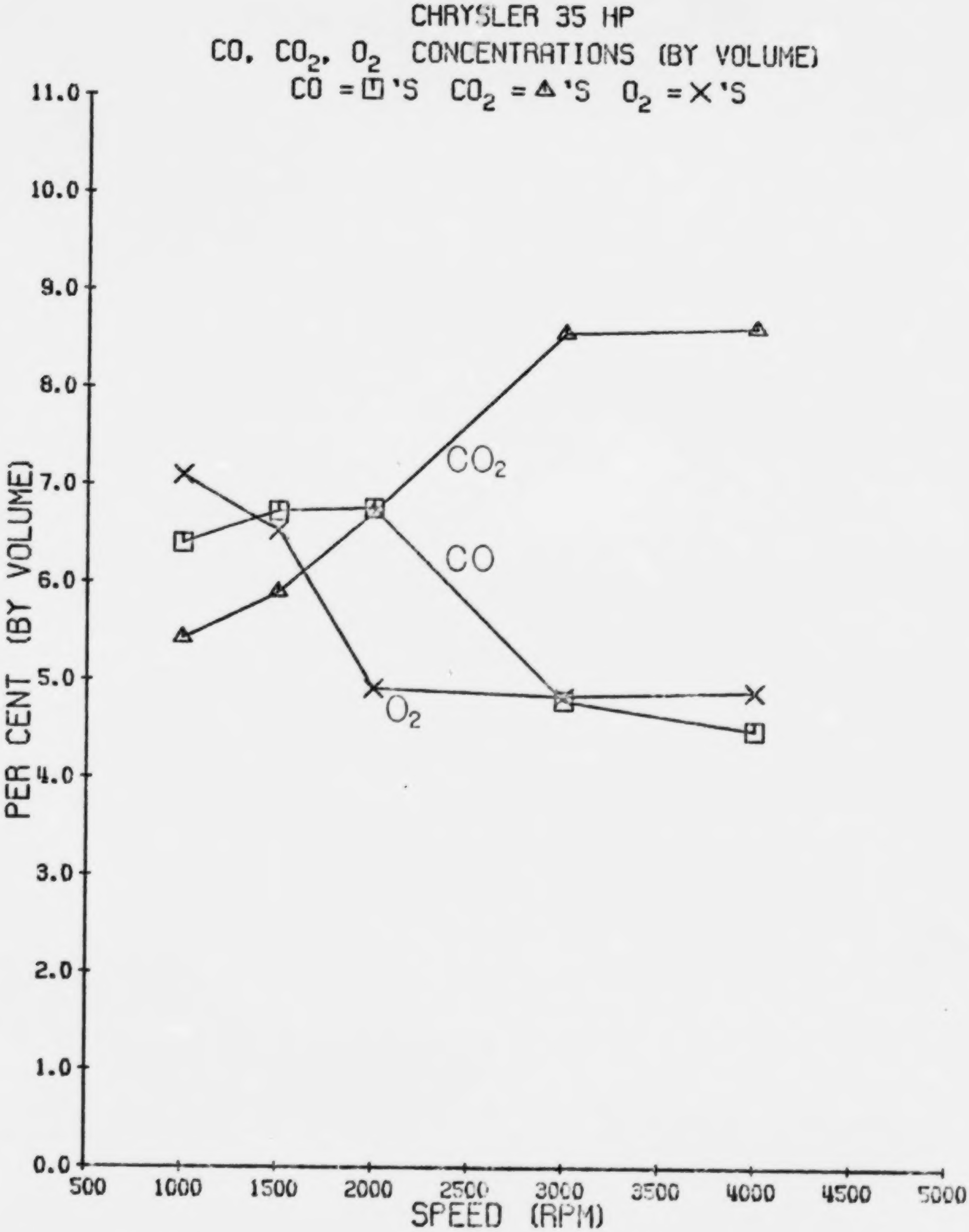

Figure 34 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 35 hp Chrysler Drained Engine

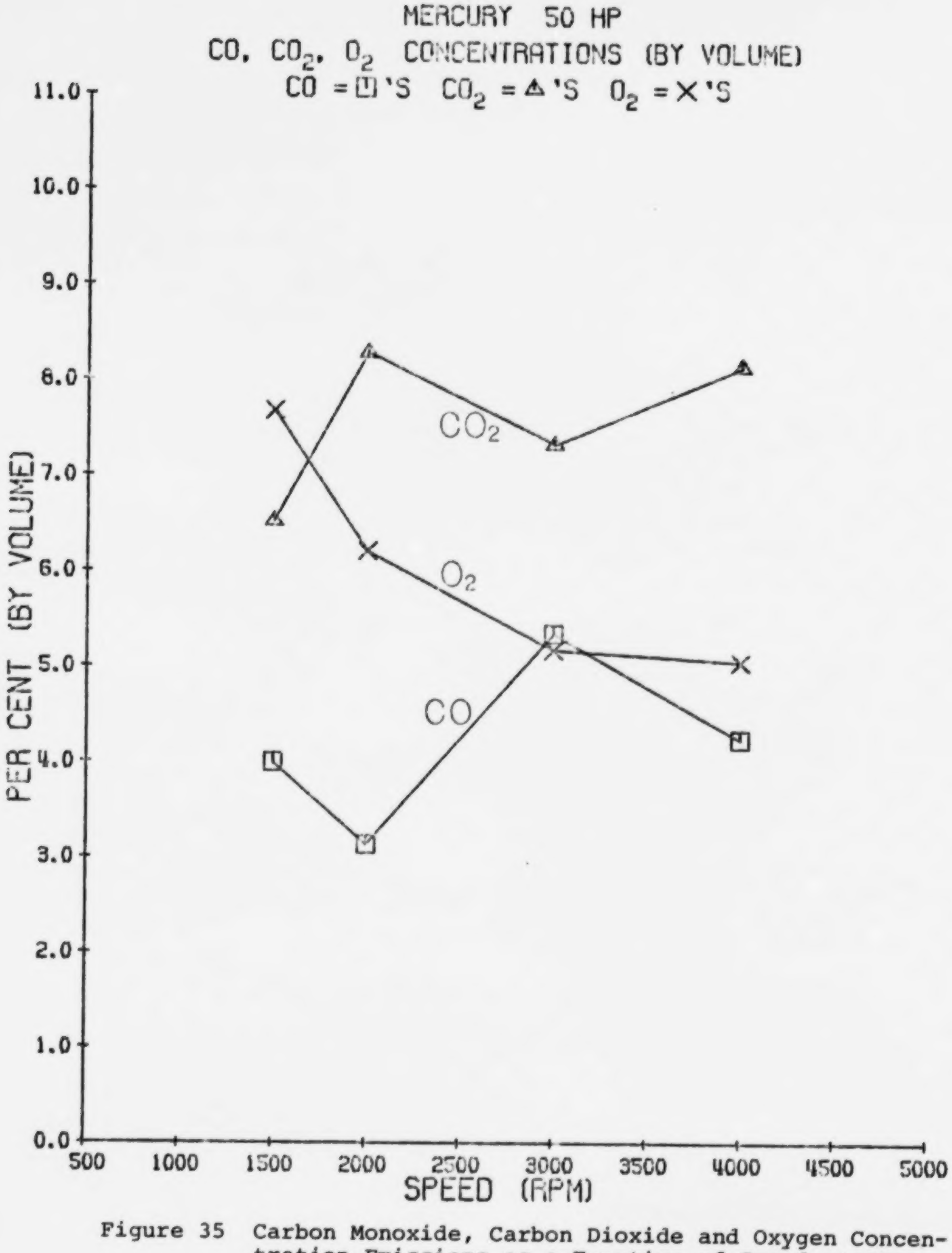

Figure 35 Carbon Monoxide, Carbon Dioxide and Oxygen Concentration Emissions as a Function of Speed at the Boat-Load Test Conditions, 50 hp Mercury Drained Engine

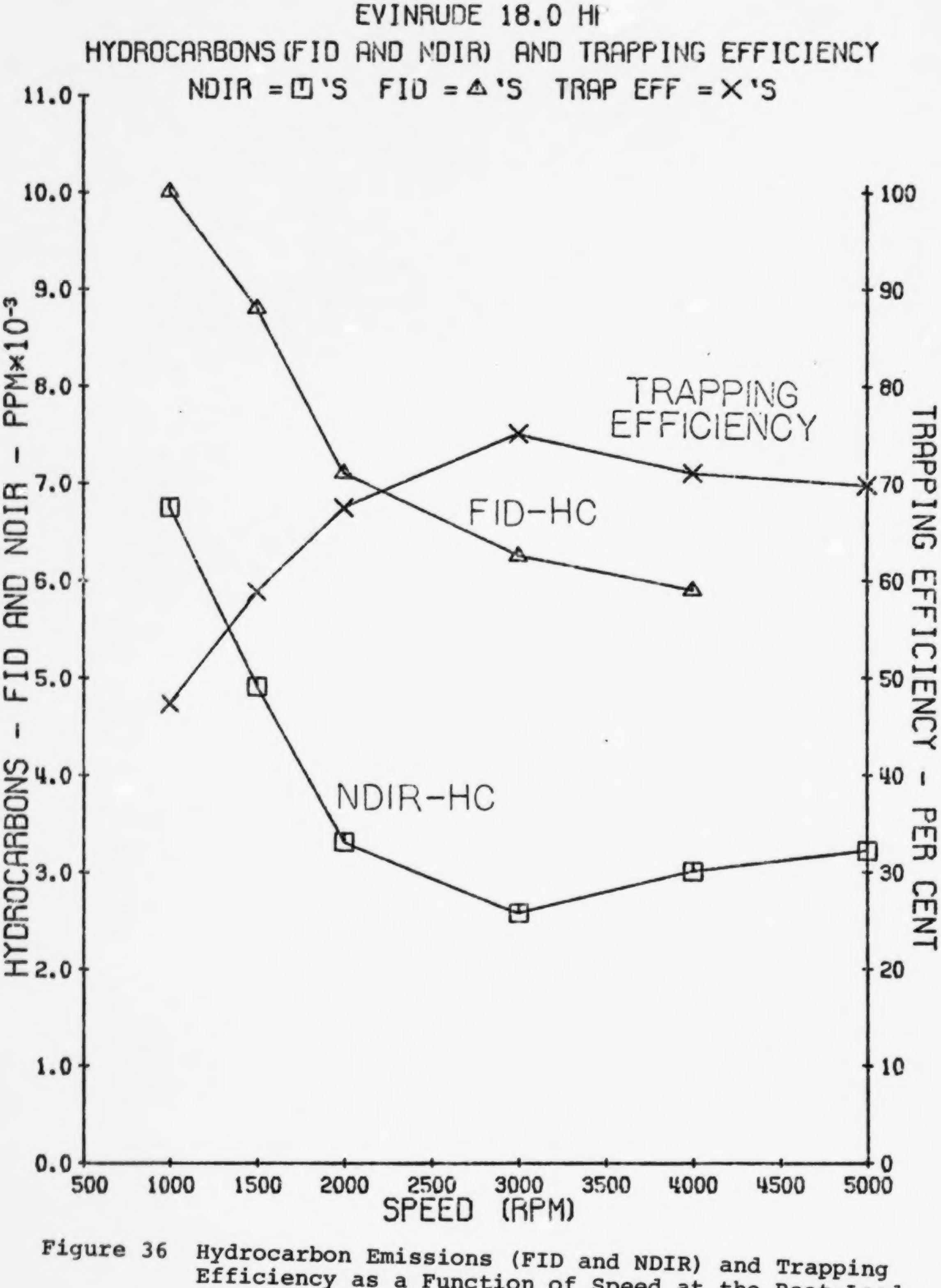

Figure 36 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 18.0 hp Evinrude Drained Engine

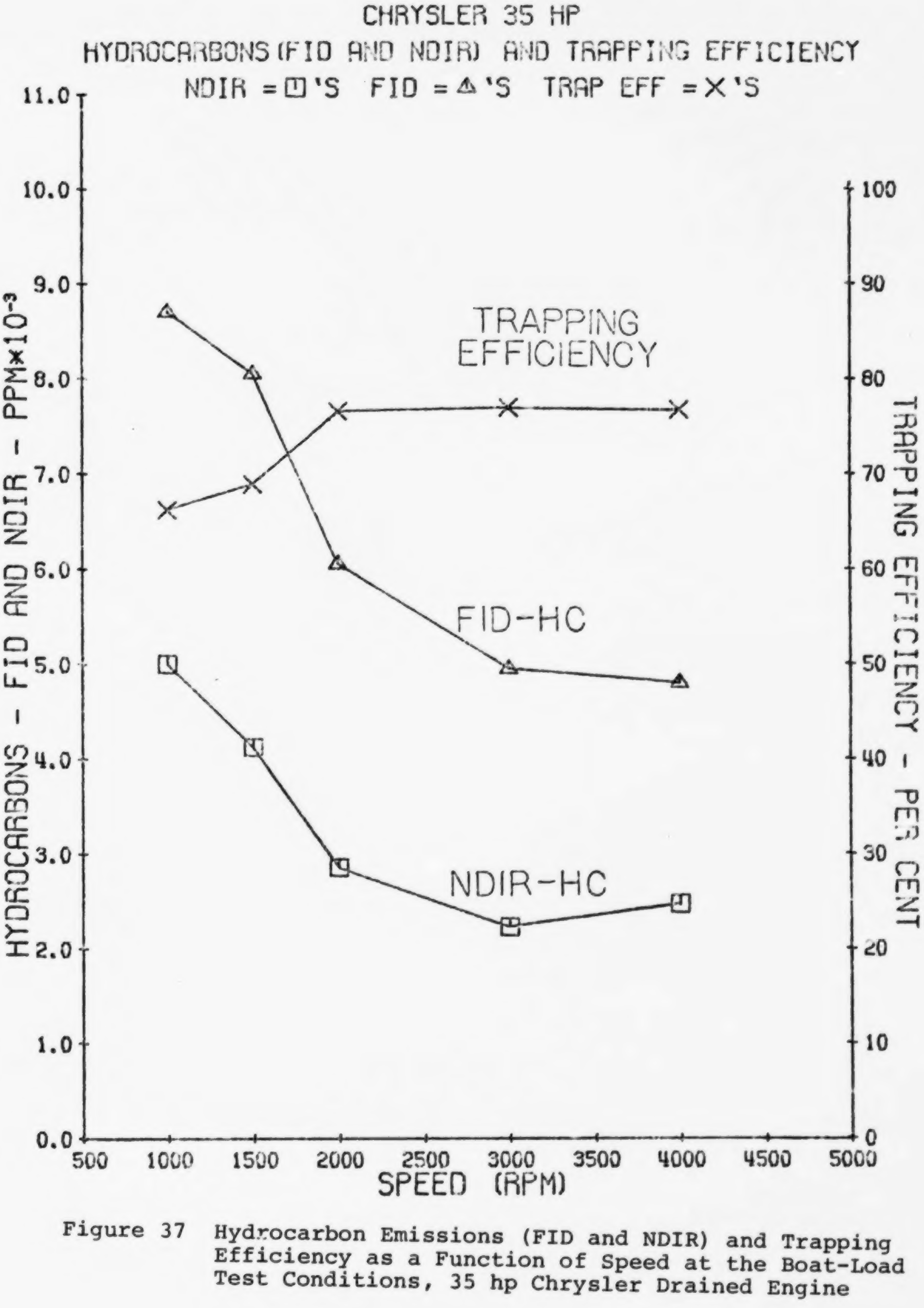

Figure 37 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 35 hp Chrysler Drained Engine

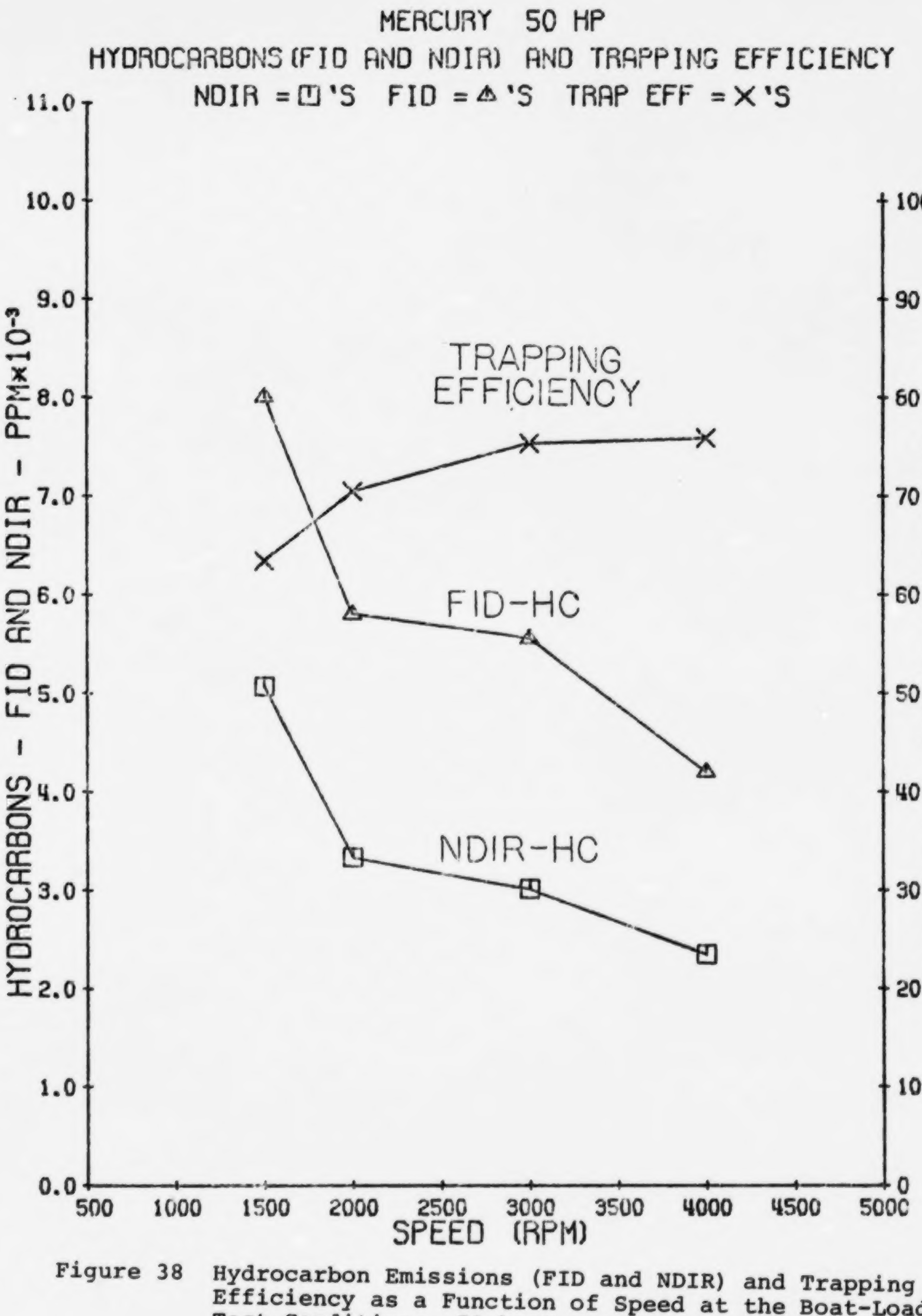

Figure 38 Hydrocarbon Emissions (FID and NDIR) and Trapping Efficiency as a Function of Speed at the Boat-Load Test Conditions, 50 hp Mercury Drained Engine

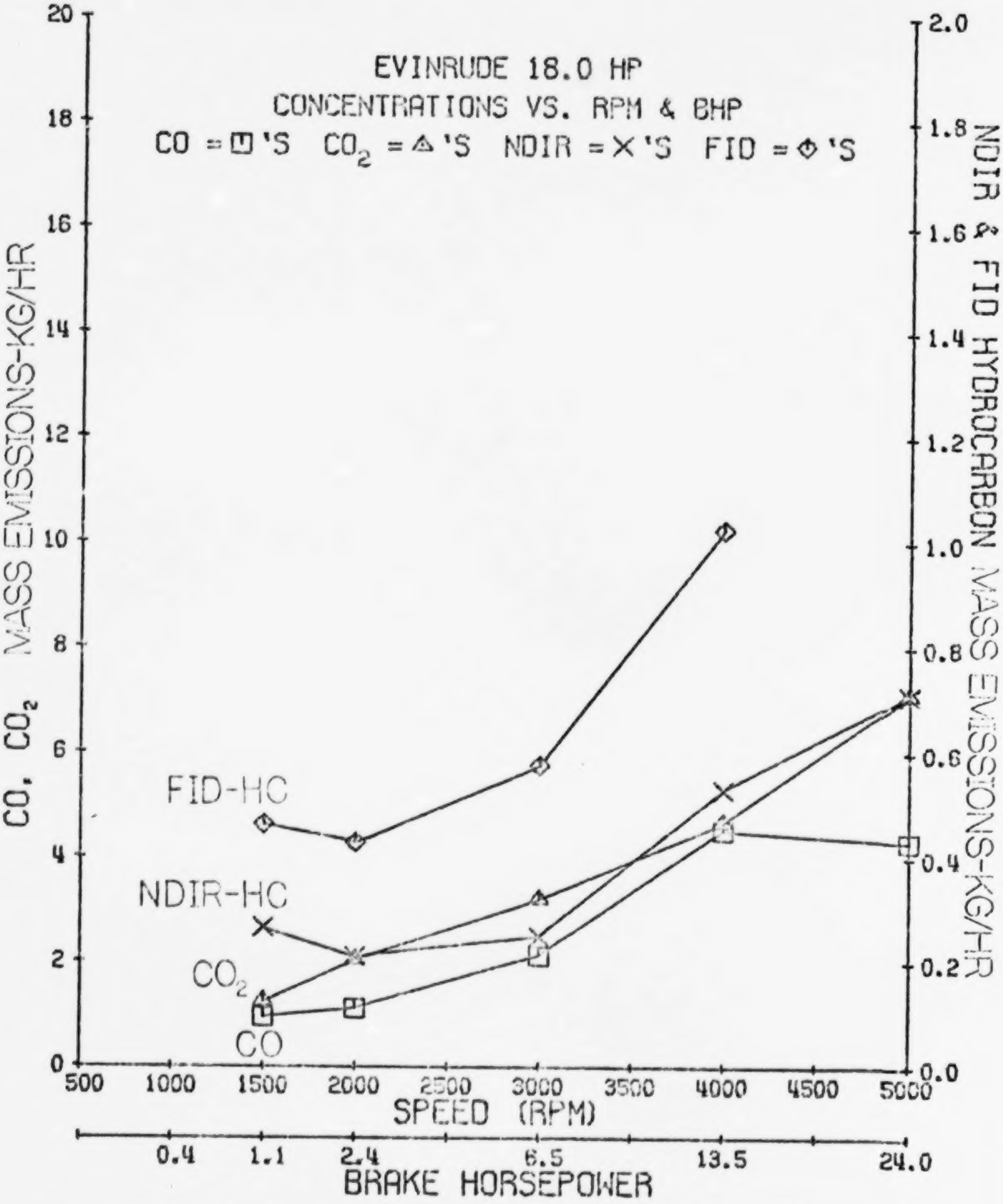

Figure 39 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 18.0 hp Evinrude Drained Engine

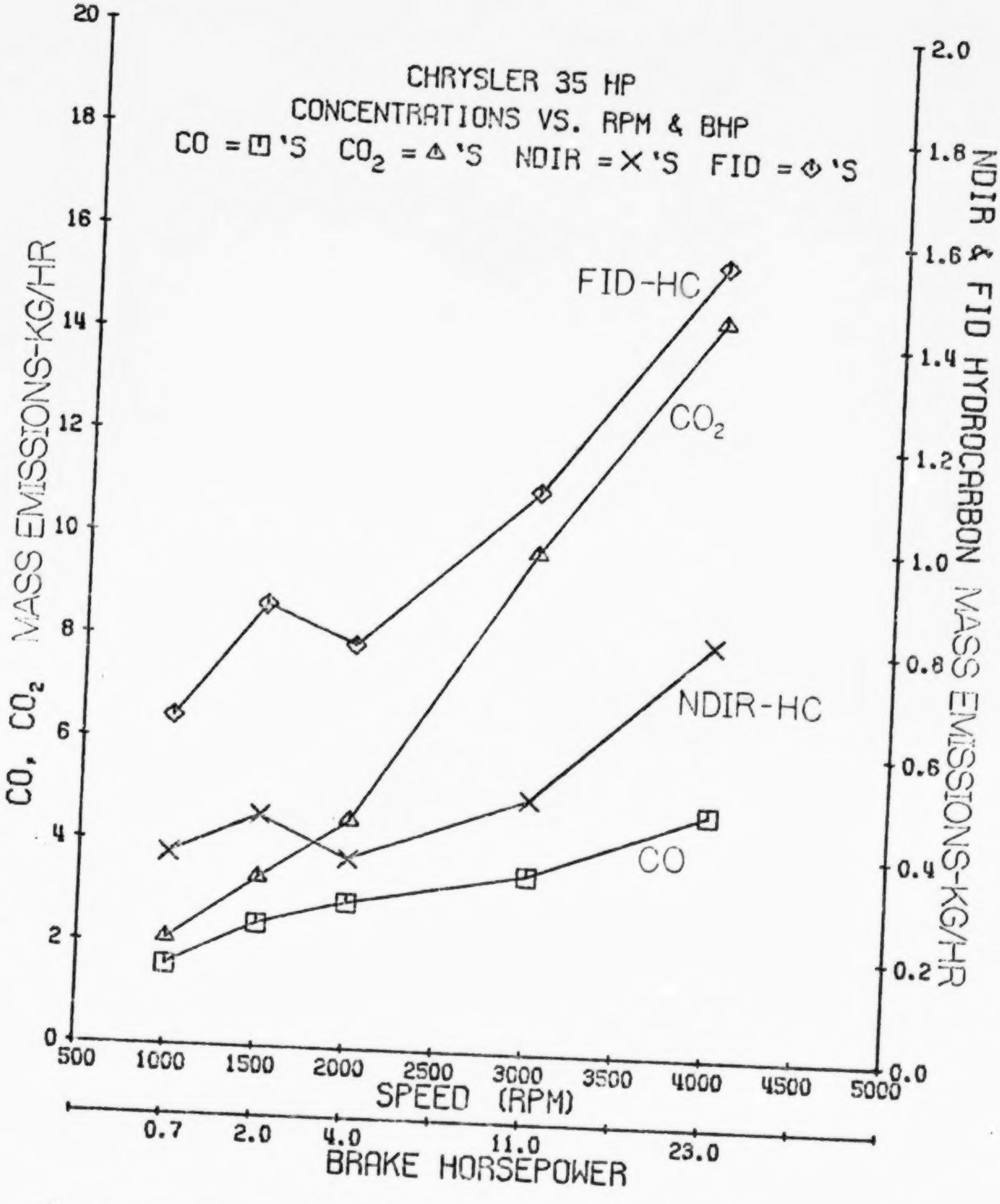

Figure 40 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 35 hp Chrysler Drained Engine

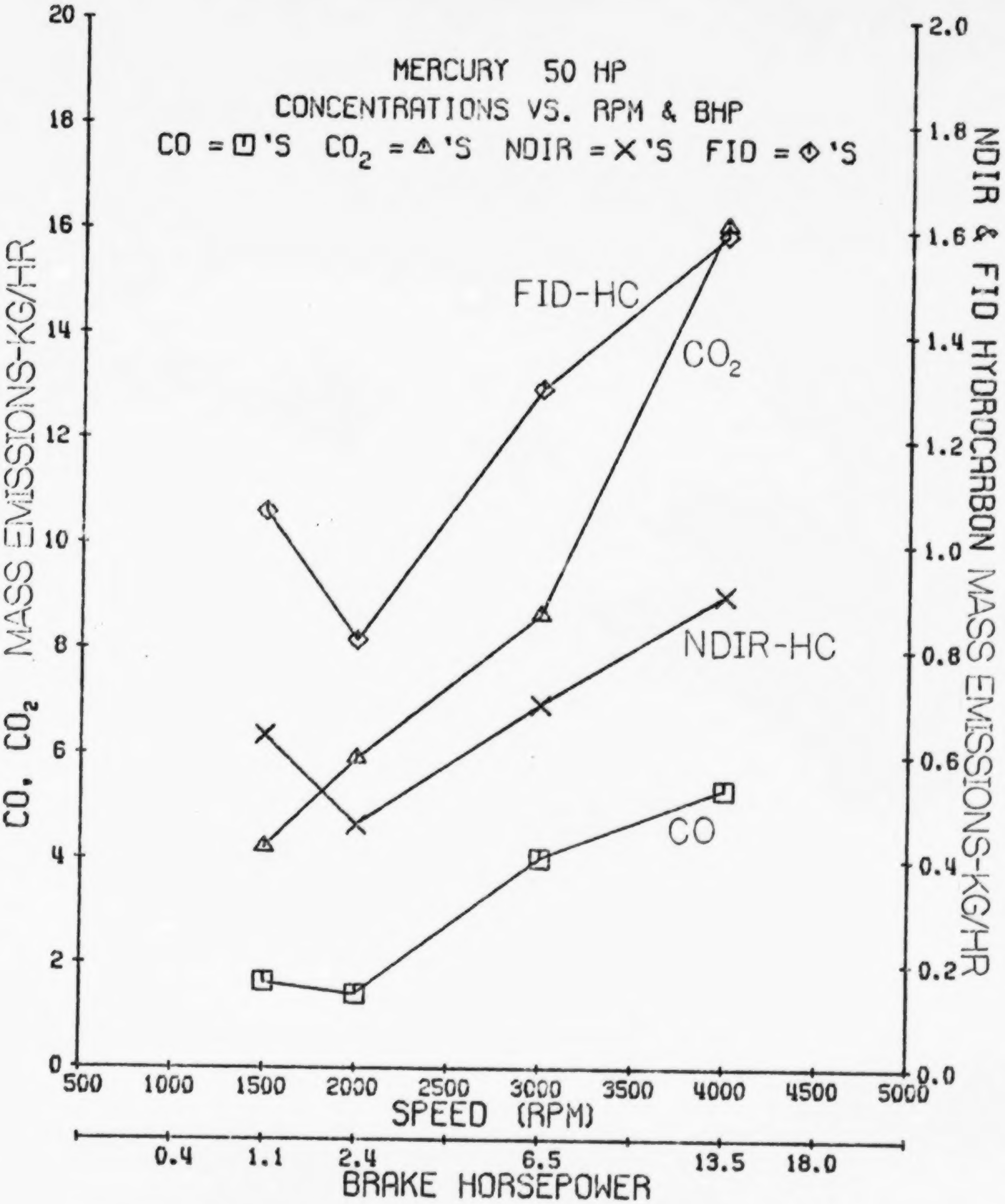

Figure 41 Mass Rate of Emissions of Carbon Monoxide, Carbon Dioxide, and NDIR and FID Hydrocarbons as a Function of Engine Speed and Brake Horsepower, 50 hp Mercury Drained Engine

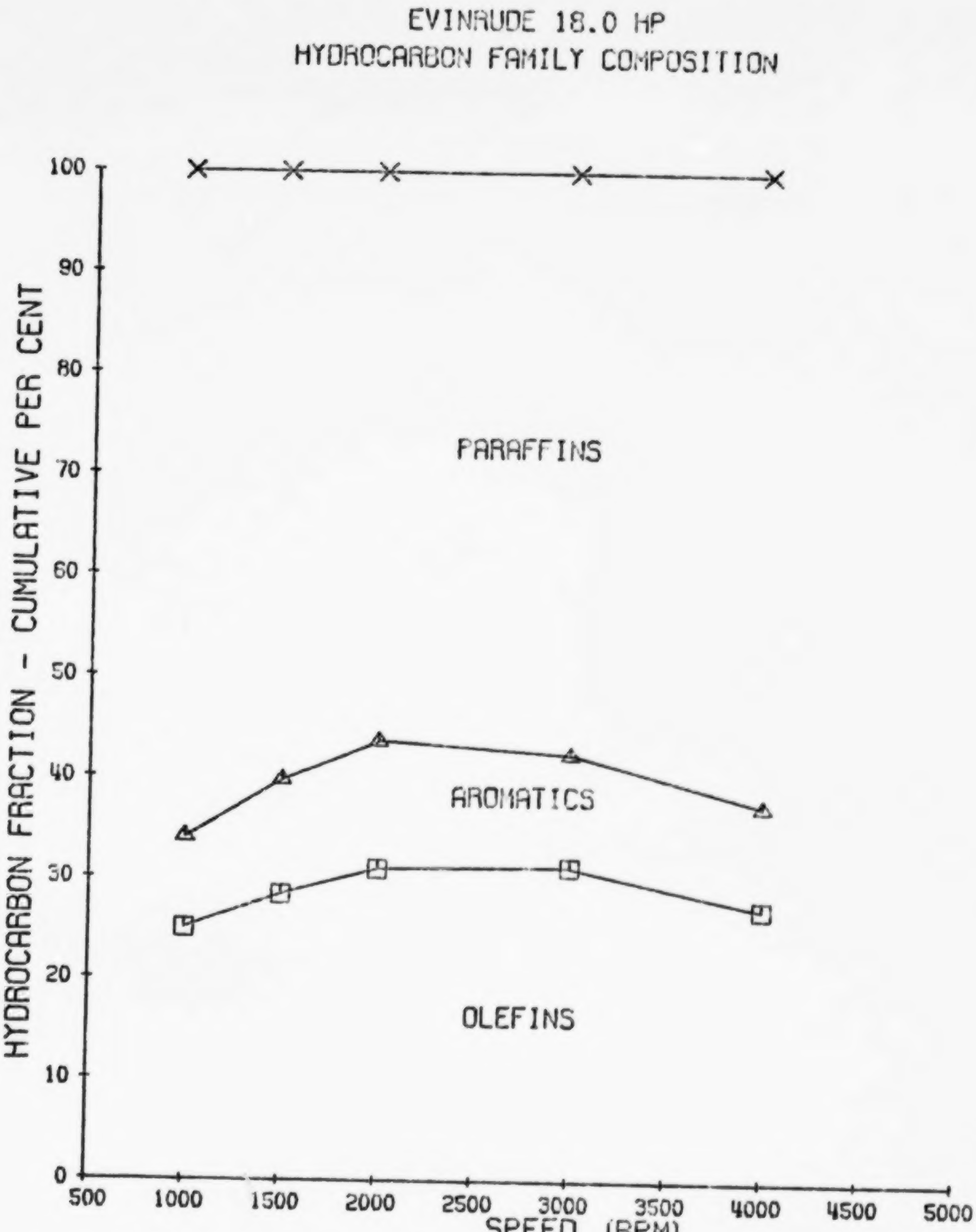

Figure 42 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 18.0 hp Evinrude Drained Engine

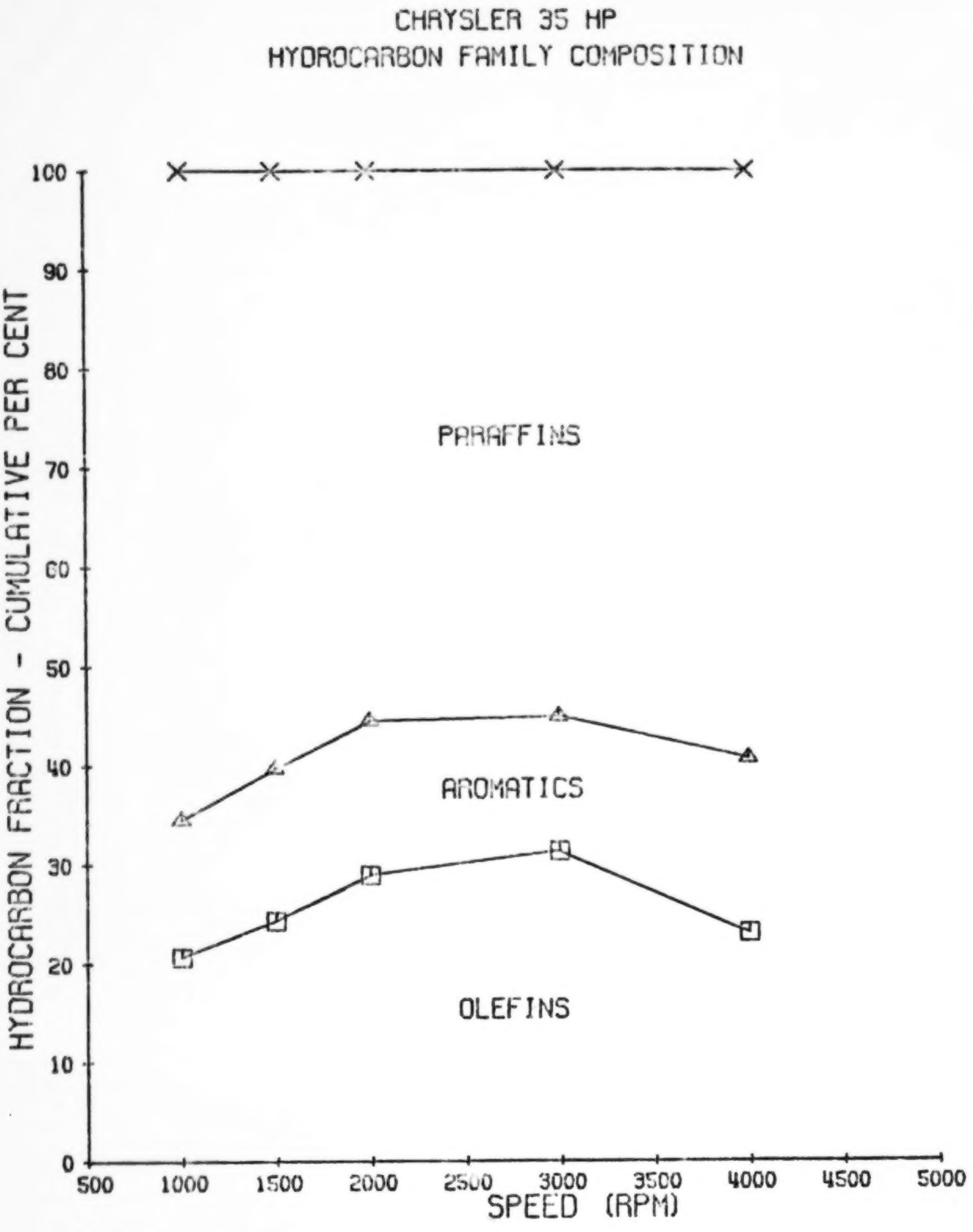

Figure 43 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 35 hp Chrysler Drained Engine

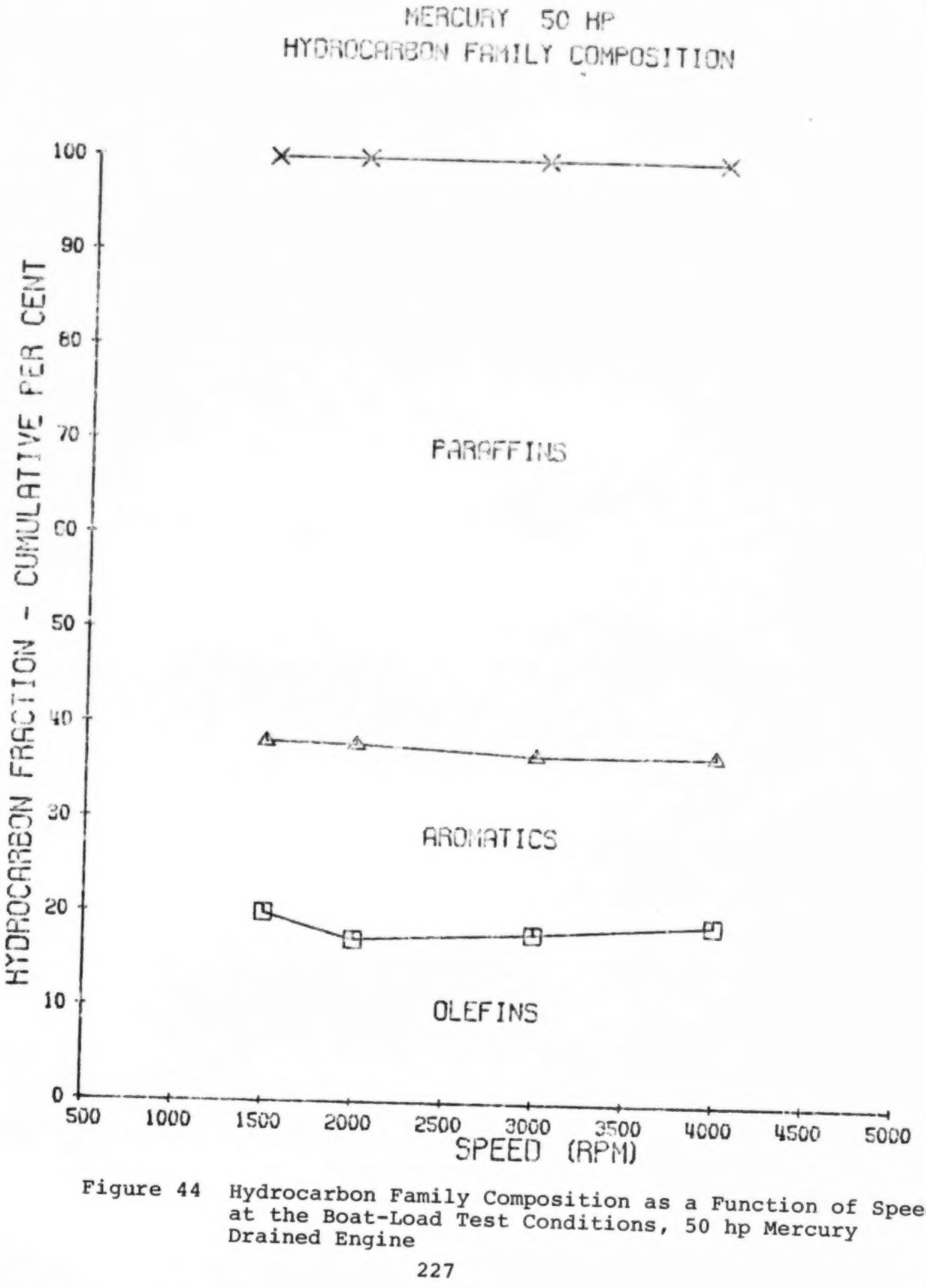

Figure 44 Hydrocarbon Family Composition as a Function of Speed at the Boat-Load Test Conditions, 50 hp Mercury Drained Engine

APPENDIX B

The Probit Analysis Program used in this study and described by Daum (33) is written in Fortran IV for use on an IBM Systems 360/30 computer. This program obtains the weighted linear regression of probits on dose employing the maximum likelihood procedure described by Finney (34). It is capable of adjusting the observed response to each dose for the response in the untreated control, and will accept zeros in either the response to a dose or in the control automatically.

The test of significance of regression is made by comparing the critical value of F_{05} with K-2 degrees of freedom with the F ratio obtained by dividing the sum of squares attributable to regression by the mean square of deviations from regression. If the calculated F ratio is less than the critical value of F_{05}, the computer prints nonsignificant regression and proceeds to read the next set of data. If the regression is significant, the computer calculates and prints the LC-values and their 95% confidence limits.

Tables 1-20 give the dose (ppm), net of linear regression, slope of the regression line, and LC-10, 20, 30, 40, 50, 60, 70, 80, 90, 95 and 99 with their upper and lower 95% confidence limits.

Appendix Table 1. --Computer analysis of goldfish exposed to leaded OME water for 24 hours

Dose (ppm)	Net response	Observed	Responded
333	100.00	6	6
222	33.33	6	2
182	16.67	6	1
167	0.00	6	0
143	0.00	6	0
133	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	11.236493		7.709999	Tabular F
Regression	1	9.934591	9.934591	30.523309	Calculated F
Deviation regression	4	1.301902	0.325476	9.488000	Chi square

Slope of the regression line = 0.001315

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	206.57	185.31	146.16
LC-20	222.14	197.56	164.21
LC-30	238.61	207.44	178.13
LC-40	258.88	216.71	189.76
LC-50	285.57	226.15	199.89
LC-60	322.91	236.45	209.22
LC-70	380.39	248.56	218.56
LC-80	487.32	264.42	229.06
LC-90	818.60	290.08	243.60
LC-95	1920.27	315.35	256.08
LC-99	---*	376.94	281.74

* Answer is beyond limits of computer program

Appendix Table 2. --Computer analysis of goldfish exposed to leaded OME water for 48 hours

Dose (ppm)	Net response	Observed	Responded
333	100.00	6	6
222	66.67	6	4
182	33.33	6	2
167	0.00	6	0
143	0.00	6	0
133	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	9.598491		7.709999	Tabular F
Regression	1	8.473579	8.473579	30.130626	Calculated F
Deviation regression	4	1.124912	0.281228	9.488000	Chi square

Slope of the regression line = 0.001422

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	187.75	171.78	134.64
LC-20	199.08	181.42	151.56
LC-30	211.40	189.07	164.61
LC-40	227.28	196.14	175.19
LC-50	248.92	203.24	183.87
LC-60	279.44	210.88	191.36
LC-70	325.91	219.71	198.47
LC-80	409.79	231.03	206.16
LC-90	649.47	248.81	216.49
LC-95	1278.18	265.70	225.13
LC-99	---*	304.46	242.35

* Answer is beyond limits of computer program

Appendix Table 3. --Computer analysis of goldfish exposed to leaded OME water for 72 hours

Dose (ppm)	Net response	Observed	Responded
333	100.00	6	6
222	83.33	6	5
182	33.33	6	2
167	16.67	6	1
143	0.00	6	0
133	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	8.884445		7.709999	Tabular F
Regression	1	8.787031	8.787031	360.811423	Calculated F
Deviation regression	4	0.097414	0.024354	9.488000	Chi square

Slope of the regression line = 0.001393

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	177.21	162.94	128.34
LC-20	186.71	171.78	143.74
LC-30	196.56	178.77	155.86
LC-40	208.94	185.22	165.95
LC-50	225.69	191.67	174.36
LC-60	249.18	198.59	181.60
LC-70	284.14	205.58	188.37
LC-80	344.08	216.77	195.59
LC-90	494.35	232.71	205.17
LC-95	782.23	247.74	213.14
LC-99	---*	281.90	228.95

* Answer is beyond limits of computer program

Appendix Table 4. --Computer analysis of goldfish exposed to leaded OME water for 96 hours

Dose (ppm)	Net response	Observed	Responded
333	100.00	6	6
222	100.00	6	6
182	66.67	6	4
167	50.00	6	3
143	0.00	6	0
133	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	8.294396		7.709999	Tabular F
Regression	1	7.692124	7.692124	51.087384	Calculated F
Deviation regression	4	0.602272	0.150568	9.488000	Chi square

Slope of the regression line = 0.001868

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	163.25	152.79	119.54
LC-20	168.50	158.49	131.32
LC-30	173.42	162.87	140.76
LC-40	179.16	166.82	149.04
LC-50	186.84	170.68	156.33
LC-60	197.83	174.73	162.54
LC-70	214.07	179.27	167.90
LC-80	239.90	184.90	173.00
LC-90	292.16	193.32	179.06
LC-95	358.81	200.88	183.72
LC-99	635.65	216.76	192.33

Appendix Table 5. --Computer analysis of goldfish exposed to non-leaded OME water for 24 hours

Dose (ppm)	Net response	Observed	Responded
333	100. 00	6	6
222	50. 00	6	3
182	16. 67	6	1
167	16. 67	6	1
143	0. 00	6	0
133	0. 00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	12. 595885		7. 709999	Tabular F
Regression	1	11. 622873	11. 622873	47. 780992	Calculated F
Deviation regression	4	0. 973012	0. 243253	9. 488000	Chi square

Slope of the regression line = 0. 001066

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	187. 89	168. 90	135. 20
LC-20	202. 82	181. 55	152. 54
LC-30	220. 73	191. 92	166. 18
LC-40	237. 31	201. 76	177. 80
LC-50	262. 31	211. 92	188. 11
LC-60	297. 37	223. 15	197. 78
LC-70	351. 57	236. 57	207. 69
LC-80	453. 16	254. 48	219. 11
LC-90	774. 79	284. 34	235. 44
LC-95	1927. 67	314. 84	249. 91
LC-99	---*	394. 13	280. 90

* Answer is beyond limits of computer program

Appendix Table 6. --Computer analysis of goldfish exposed to non-leaded OME water for 48 hours

Dose (ppm)	Net response	Observed	Responded
333	100.00	6	6
222	66.67	6	4
182	50.00	6	3
167	16.67	6	1
143	0.00	6	0
133	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	12.198762		7.709999	Tabular F
Regression	1	11.104588	11.104588	40.595327	Calculated F
Deviation regression	4	1.094174	0.273544	9.488000	Chi square

Slope of the regression line = 0.001104

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	173.85	158.13	127.10
LC-20	185.49	168.76	142.65
LC-30	197.30	177.36	154.93
LC-40	211.62	185.44	165.38
LC-50	230.43	193.68	174.50
LC-60	256.44	202.69	182.84
LC-70	295.34	213.31	191.14
LC-80	363.53	227.23	200.46
LC-90	544.56	249.86	213.48
LC-95	938.55	272.25	224.78
LC-99	---*	327.24	248.34

* Answer is beyond limits of computer program

Appendix Table 7. --Computer analysis of goldfish exposed to non-leaded OME water for 72 hours

Dose (ppm)	Net response	Observed	Responded
333	100. 00	6	6
222	66. 67	6	4
182	66. 67	6	4
167	33. 33	6	2
143	0. 00	6	0
133	0. 00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	14. 402369		7. 709999	Tabular F
Regression	1	11. 881187	11. 881197	18. 850185	Calculated F
Deviation regression	4	2. 521182	0. 630295	9. 488000	Chi square

Slope of the regression line = 0. 001004

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	164. 50	149. 50	120. 23
LC-20	175. 52	159. 98	135. 06
LC-30	186. 44	168. 49	146. 96
LC-40	199. 47	176. 52	157. 30
LC-50	216. 51	184. 74	166. 49
LC-60	240. 12	193. 77	174. 97
LC-70	275. 42	204. 46	183. 44
LC-80	337. 00	218. 58	193. 00
LC-90	497. 64	241. 72	206. 42
LC-95	832. 55	264. 88	218. 16
LC-99	---*	322. 90	242. 95

* Answer is beyond limits of computer program

Appendix Table 8. --Computer analysis of goldfish exposed to non-leaded OME water for 96 hours

Dose (ppm)	Net response	Observed	Responded
333	100. 00	6	6
222	100. 00	6	6
182	83. 33	6	5
167	50. 00	6	3
143	0. 00	6	0
133	0. 00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	5. 464023		7. 709999	Tabular F
Regression	1	5. 354765	5. 354765	196. 041718	Calculated F
Deviation regression	4	0. 109258	0. 027314	9. 488000	Chi square

Slope of the regression line = 0. 002343

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	163. 47	153. 75	98. 69
LC-20	167. 24	158. 33	111. 84
LC-30	170. 70	161. 79	123. 39
LC-40	174. 84	164. 88	134. 70
LC-50	181. 05	167. 87	145. 88
LC-60	192. 39	170. 98	155. 88
LC-70	214. 03	174. 43	163. 35
LC-80	255. 63	178. 65	168. 81
LC-90	362. 44	184. 85	173. 99
LC-95	562. 99	189. 94	177. 53
LC-99	---*	201. 46	183. 67

* Answer is beyond limits of computer program

Appendix Table 9. --Computer analysis of goldfish exposed to toluene-solution OME water for 24 hours

Dose (ppm)	Net response	Observed	Responded
81	100. 00	6	6
40	33. 33	6	2
30	33. 33	6	2
20	16. 67	6	1
13	0. 00	6	0
8	0. 00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	9. 644886		7. 709999	Tabular F
Regression	1	8. 121691	8. 121691	21. 328040	Calculated F
Deviation regression	4	1. 523195	0. 380799	9. 488000	Chi square

Slope of the regression line = 0. 061923

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	30. 42	20. 90	-5. 25
LC-20	39. 48	28. 00	12. 66
LC-30	49. 46	33. 13	22. 12
LC-40	60. 33	37. 50	27. 85
LC-50	71. 72	41. 59	31. 99
LC-60	83. 75	45. 68	35. 49
LC-70	97. 02	50. 06	38. 83
LC-80	112. 84	55. 18	42. 45
LC-90	135. 06	62. 29	47. 20
LC-95	153. 55	68. 16	50. 97
LC-99	188. 42	79. 16	57. 86

Appendix Table 10. --Computer analysis of goldfish exposed to toluene-solution OME water for 48 hours

Dose (ppm)	Net response	Observed	Responded
81	100.00	6	6
40	83.33	6	5
30	66.67	6	4
20	33.33	6	2
13	0.00	6	0
8	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	13.015258		7.709999	Tabular F
Regression	1	11.541441	11.541441	31.323932	Calculated F
Deviation regression	4	1.473818	0.368454	9.488000	Chi square

Slope of the regression line = 0.104062

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	21.38	15.30	-0.70
LC-20	25.18	19.53	8.17
LC-30	28.54	22.58	13.95
LC-40	32.07	25.18	18.23
LC-50	36.01	27.62	21.58
LC-60	40.52	30.05	24.38
LC-70	45.78	32.66	26.92
LC-80	52.31	35.70	29.54
LC-90	61.72	39.93	32.80
LC-95	69.67	43.42	35.32
LC-99	84.78	49.97	39.84

Appendix Table 11. --Computer analysis of goldfish exposed to toluene-solution OME water for 72 hours

Dose (ppm)	Net response	Observed	Responded
81	100.00	6	6
40	100.00	6	6
30	66.67	6	4
20	33.33	6	2
13	0.00	6	0
8	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	12.146147		7.709999	Tabular F
Regression	1	11.062539	11.062539	40.835971	Calculated F
Deviation regression	4	1.083607	0.270902	9.488000	Chi square

Slope of the regression line = 0.147875

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	21.55	16.67	3.87
LC-20	24.29	19.64	10.25
LC-30	26.68	21.79	14.44
LC-40	29.14	23.62	17.59
LC-50	31.85	25.33	20.13
LC-60	34.95	27.05	22.27
LC-70	38.62	28.88	24.23
LC-80	43.21	31.03	26.21
LC-90	49.90	34.00	28.69
LC-95	55.58	36.46	30.48
LC-99	66.45	41.07	33.73

Appendix Table 12. --Computer analysis of goldfish exposed to toluene-solution OME water for 96 hours

Dose (ppm)	Net response	Observed	Responded
81	100.00	6	6
40	100.00	6	6
30	66.67	6	4
20	50.00	6	3
13	16.67	6	1
8	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	13.322929		7.709999	Tabular F
Regression	1	11.862186	11.862186	32.482590	Calculated F
Deviation regression	4	1.460744	0.365186	9.488000	Chi square

Slope of the regression line = 0.112125

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	17.10	11.37	-3.88
LC-20	20.51	15.30	4.31
LC-30	23.46	18.12	9.73
LC-40	26.52	20.54	13.82
LC-50	29.95	22.80	17.07
LC-60	33.91	25.06	19.79
LC-70	38.60	27.48	22.26
LC-80	44.47	30.31	24.76
LC-90	52.99	34.23	27.84
LC-95	60.20	37.47	30.21
LC-99	73.95	43.55	34.45

Appendix Table 13. --Computer analysis of goldfish exposed to xylene-solution OME water for 24 hours

Dose (ppm)	Net response	Observed	Responded
62	100. 00	6	6
40	100. 00	6	6
30	33. 33	6	2
24	16. 67	6	1
18	0. 00	6	0
5	0. 00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	9. 011104		7. 709999	Tabular F
Regression	1	8. 058059	8. 058059	33. 820254	Calculated F
Deviation regression	4	0. 953045	0. 238261	9. 488000	Chi square

Slope of the regression line = 0. 201487

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	27. 96	24. 19	11. 40
LC-20	30. 12	26. 38	17. 59
LC-30	32. 19	27. 95	21. 54
LC-40	34. 53	29. 30	24. 34
LC-50	37. 26	30. 55	26. 42
LC-60	40. 43	31. 81	28. 05
LC-70	44. 16	33. 16	29. 47
LC-80	48. 78	34. 73	30. 86
LC-90	55. 44	36. 91	32. 55
LC-95	61. 06	38. 72	33. 82
LC-99	71. 74	48. 10	36. 07

Appendix Table 14. --Computer analysis of goldfish exposed to xylene-solution OME water for 48 hours

Dose (ppm)	Net response	Observed	Responded
62	100.00	6	6
40	100.00	6	6
30	66.67	6	4
24	50.00	6	3
18	16.67	6	1
5	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	8.794731		7.709999	Tabular F
Regression	1	8.336710	8.336710	72.806298	Calculated F
Deviation regression	4	0.458021	0.114505	9.488000	Chi square

Slope of the regression line = 0.138894

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	21.03	15.87	-5.08
LC-20	23.52	19.04	4.18
LC-30	25.69	21.32	10.48
LC-40	28.07	23.27	15.35
LC-50	31.01	25.10	19.16
LC-60	34.82	26.92	22.12
LC-70	39.68	28.87	24.50
LC-80	45.97	31.16	26.68
LC-90	55.23	34.32	29.17
LC-95	63.08	36.94	31.02
LC-99	78.04	41.85	34.26

Appendix Table 15. --Computer analysis of goldfish exposed to xylene-solution OME water for 72 hours

Dose (ppm)	Net response	Observed	Responded
62	100. 00	6	6
40	100. 00	6	6
30	100. 00	6	6
24	66. 67	6	4
18	33. 33	6	2
5	0. 00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	6. 393179		7. 709999	Tabular F
Regression	1	5. 935949	5. 935949	51. 929578	Calculated F
Deviation regression	4	0. 457231	0. 114308	9. 488000	Chi square

Slope of the regression line = 0. 205018

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	18. 77	14. 47	-17. 21
LC-20	20. 32	16. 62	-6. 60
LC-30	21. 64	18. 16	0. 86
LC-40	23. 07	19. 49	6. 92
LC-50	24. 95	20. 72	12. 04
LC-60	27. 83	21. 96	16. 17
LC-70	32. 33	23. 28	19. 16
LC-80	38. 93	24. 83	21. 33
LC-90	49. 09	26. 97	23. 33
LC-95	57. 82	28. 74	24. 65
LC-99	74. 48	32. 07	26. 83

Appendix Table 16. --Computer analysis of goldfish exposed to xylene-solution OME water for 96 hours

Dose (ppm)	Net response	Observed	Responded
62	100.00	6	6
40	100.00	6	6
30	100.00	6	6
24	83.33	6	5
18	66.67	6	4
5	0.00	6	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	7.778989		7.709999	Tabular F
Regression	1	7.133426	7.133426	44.199742	Calculated F
Deviation regression	4	0.645563	0.161391	9.488000	Chi square

Slope of the regression line = 0.181939

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	15.10	9.90	-17.46
LC-20	16.85	12.32	-8.73
LC-30	18.28	14.06	-2.60
LC-40	19.70	15.55	2.44
LC-50	21.31	16.94	6.86
LC-60	23.42	18.34	10.79
LC-70	26.45	19.83	14.20
LC-80	31.11	21.57	17.11
LC-90	38.86	23.99	19.84
LC-95	45.80	25.98	21.56
LC-99	59.32	29.73	24.26

Appendix Table 17. --Computer analysis of goldfish exposed to 1, 3, 5 trimethylbenzene-solution OME water for 24 hours

Dose (ppm)	Net response	Observed	Responded
28	100.00	8	8
19	25.00	8	2
14	12.50	8	1
10	0.00	8	0
4	0.00	8	0
2	0.00	8	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	11.728461		7.709999	Tabular F
Regression	1	10.413758	10.413758	31.683993	Calculated F
Deviation regression	4	1.314703	0.328676	9.488000	Chi square

Slope of the regression line = 0.248006

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	18.19	15.41	8.42
LC-20	19.99	17.18	12.24
LC-30	21.63	18.46	14.65
LC-40	23.37	19.55	16.38
LC-50	25.26	20.57	17.72
LC-60	27.37	21.59	18.85
LC-70	29.79	22.69	19.89
LC-80	32.77	23.97	20.97
LC-90	37.03	25.74	22.33
LC-95	40.62	27.21	23.38
LC-99	47.45	29.95	25.26

Appendix Table 18. --Computer analysis of goldfish exposed to 1, 3, 5 trimethylbenzene-solution OME water for 48 hours

Dose (ppm)	Net response	Observed	Responded
28	100. 00	8	8
19	87. 50	8	7
14	25. 00	8	2
10	0. 00	8	0
4	0. 00	8	0
2	0. 00	8	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	8. 883020		7. 709999	Tabular F
Regression	1	8. 818447	8. 818447	546. 262890	Calculated F
Deviation regression	4	0. 064573	0. 016143	9. 488000	Chi square

Slope of the regression line = 0. 392352

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	14. 87	12. 90	6. 11
LC-20	15. 85	14. 02	9. 11
LC-30	16. 71	14. 83	11. 12
LC-40	17. 63	15. 52	12. 65
LC-50	18. 71	16. 17	13. 85
LC-60	20. 02	16. 81	14. 83
LC-70	21. 63	17. 50	15. 67
LC-80	23. 69	18. 31	16. 47
LC-90	26. 74	19. 43	17. 40
LC-95	29. 33	20. 36	18. 09
LC-99	34. 29	22. 10	19. 28

Appendix Table 19. --Computer analysis of goldfish exposed to 1, 3, 5 trimethylbenzene-solution OME water for 72 hours

Dose (ppm)	Net response	Observed	Responded
28	100.00	8	8
19	100.00	8	8
14	50.00	8	4
10	12.50	8	1
4	0.00	8	0
2	0.00	8	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	10.453808		7.709999	Tabular F
Regression	1	9.821587	9.821587	62.140248	Calculated F
Deviation regression	4	0.632221	0.158055	9.488000	Chi square

Slope of the regression line = 0.342965

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	12.07	9.92	3.01
LC-20	13.15	11.20	6.15
LC-30	14.07	12.13	8.26
LC-40	15.04	12.92	9.90
LC-50	16.15	13.65	11.21
LC-60	17.49	14.39	12.30
LC-70	19.14	15.18	13.24
LC-80	21.27	16.11	14.15
LC-90	24.41	17.39	15.22
LC-95	27.10	18.45	16.01
LC-99	32.25	20.44	17.39

Appendix Table 20. --Computer analysis of goldfish exposed to 1, 3, 5 trimethylbenzene-solution OME water for 96 hours --

Dose (ppm)	Net response	Observed	Responded
28	100.00	8	8
19	100.00	8	8
14	62.50	8	5
10	25.00	8	2
4	0.00	8	0
2	0.00	8	0

Analysis of linear regression

Source of variation	df	Sum of squares	Mean square		
Total	5	11.500106		7.709999	Tabular F
Regression	1	10.906775	10.906775	73.529120	Calculated F
Deviation regression	4	0.593331	0.148333	9.488000	Chi square

Slope of the regression line = 0.300903

Lethal concentrations with upper and lower 95% confidence limits in ppm

	Upper limit	Lethal concentration	Lower limit
LC-10	10.64	8.26	1.15
LC-20	11.85	9.72	4.46
LC-30	12.86	10.78	6.70
LC-40	13.88	11.68	8.45
LC-50	15.05	12.52	9.89
LC-60	16.43	13.36	11.10
LC-70	18.15	14.26	12.17
LC-80	20.36	15.32	13.21
LC-90	23.65	16.78	14.44
LC-95	26.46	17.99	15.35
LC-99	31.86	20.25	16.95